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SPECIFIC AIR POLLUTANTS FROM MUNITIONS PROCESSING AND THEIR ATM--ETC(U)

JAN 78 B H CARPENTER, R LIEPINS, J SICKLES

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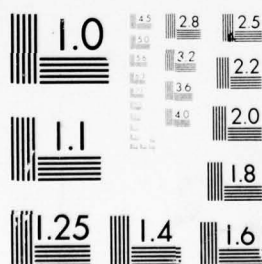
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(6) SPECIFIC AIR POLLUTANTS FROM MUNITIONS PROCESSING
AND THEIR ATMOSPHERIC BEHAVIOR,

VOLUME 4,

OPEN BURNING AND INCINERATION OF WASTE MUNITIONS,

FINAL REPORT

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This work is directed toward better definition of the specific air pollutants generated from the production of RDX and TNT, together with their attendant raw material manufacture and recovery processes, and the incineration of offgrade and used materials. Plant visits were made to discuss operations and acquire available data. These data, together with survey reports by the USAEHA and technology reports from the arsenals, were used to develop a state- of-knowledge emissions inventory projected to "mobilization" production rates.		

(Abstract cont'd)

Individual emission sources were characterized to the extent possible. The considerable data gaps were identified and flagged for further investigation. A methodology was applied to develop estimates of concentrations of the various compounds that might arise in the air over the plant. The chemical and toxicological characteristics of known emitted compounds were used and their relevant chemical reactivity under photochemical and at ground state was reviewed by literature search. The various possible transformation processes were catalogued. Data gaps were indicated.

Based on this assessment, the following recommendations were developed.

TNT PROCESS

Source sampling of a single continuous process line should be conducted in depth to provide data in the identify of pollutants and their relation to process parameters and source controls. These data are prerequisite to further assessment of the air chemistry through dispersion and photochemical modeling.

RDX PROCESS

Further development of currently available process and source emissions data is needed. Source characteristics and process conditions developed herein should be defined and confirmed for use in future assessments. Specific compounds in source emissions need fugitive emissions and emissions from process vents should both be sampled and tested.

RDX CHEMISTRY

Assessment of the potential pollutant reactions in air indicates that known carcinogens may be formed: N-nitrosodimethylamine from dimethylamine emissions and N-nitrosomethylamine from methylamine emissions. Modeling will provide further guidance on the emissions likely to be present in the environment and enable investigators to select test methodology for individual compounds. Sampling should then be employed to define further the emission rates for organic compounds and to quantify each nitrogen oxide species. Further assessment of the potential for formation of toxic levels of these substances using photochemical-diffusion modeling is recommended as the next immediate effort in order to set guidelines for laboratory studies and ambient air testing.

INCINERATION

The trend toward air curtain incinerators, instead of the better controlled SITPA II and Rotary Kiln incinerators, presents the possibility that emissions problems will still exist, since such problems persist among municipal incinerators. A strong effort in computer modeling of combustion product generation in the incineration of explosives and propellants is needed to determine the fuel and air feed rates and temperatures required to optimize incinerator operation and minimize pollutant emissions.

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ABBREVIATIONS AND ACRONYMS

AAP	Army Ammunition Plant
HAAP	Holston Army Ammunition Plant
JAAP	Joliet Army Ammunition Plant
RAAP	Radford Army Ammunition Plant
NAAP	Newport Army Ammunition Plant
VAAP	Volunteer Army Ammunition Plant
USAEHA	United States Army Environmental Hygiene Agency
TNT	Trinitrotoluene
RDX	Cyclotrimethylenetrinitramine
NEDS	National Emissions Data System
TPD	Tons per day
SPS	Source Performance Standards
NAAQS	National Ambient Air Quality Standards
N&P	Nitration and Purification
SA	Spent Acid Tanks
ST	Settling Tanks
NAC/SAC	Nitric Acid Concentration/ Sulfuric Acid Concentration
DSN	Direct Strong Nitric Acid Plant
RWP	Red Water Processing
FB	Finishing Building
AOP	Ammonia Oxidation Plant
NAC	Nitric Acid Concentration
SAC	Sulfuric Acid Concentrator
SAR	Sulfuric Acid Regeneration
TNM	Tetranitromethane
SC/SA	Single Contact/Single Absorption Acid Plant
DC/DA	Double Contact/Double Absorption Acid Plant
CAR	Carcinogenic effects - producing cancer
CNS	Central nervous system effects
EYE	Eye effects
GIT	Gastrointestinal tract effects
ham	hamster
hmn	human
ihl	Inhalation

ABBREVIATIONS AND ACRONYMS (cont'd)

ims	Intramuscular
ipl	Intraplueral
ipr	Intraperitoneal
IRR	Irritant effects
itr	Intratracheal
IVN	Intravenous
MAN	Man
MTH	Mouth effects
MUT	Mutagenic effects
mus	mouse
NEO	Neoplastic effects
orl	Oral
par	Parenteral
PNS	Peripheral nervous system effects
PSY	Psychotropic effects
PUL	Pulmonary system effects
rat	Rat
rbt	Rabbit
SKN	Skin effects
scu	Subcutaneous
TER	Teratogenic effects
unk	Unreported route
wmn	Woman

SPECIFIC AIR POLLUTANTS FROM MUNITIONS PROCESSING
AND THEIR ATMOSPHERIC BEHAVIOR
VOLUME 4 -- OPEN BURNING AND INCINERATION OF WASTE MUNITIONS
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6.0 EMISSIONS ASSESSMENT FROM PLANT OPERATIONS

6.C.0 INTRODUCTION

The Office of the Army Surgeon General is responsible for development of health and environmental guidelines governing emissions of military-related compounds. The U.S. Army Medical Bioengineering Research and Development Laboratory (USAMBRDL) has reported an evaluation of the air pollution potential of seven substances emitted at Army Ammunition Plants (AAP's) for which emissions and air quality standards currently do not exist.¹ The evaluation provides a background for further investigations of possible needs for appropriate air quality standards.

This study provides a continuation of the effort to establish a data base from which either discharge or ambient standards for air pollutants not addressed by the Environmental Protection Agency can be recommended. The study is limited to the production of trinitrotoluene (TNT); the production of cyclotrimethylenetrinitramine (RDX); and the incineration of waste materials. The investigation required consideration of the nature of the explosives manufacturing processes and the emissions controls applied, the possible emissions, their potential for chemical reaction and photochemical reaction, and their toxicity.

APPROACH

Visits were made to army ammunition plants at Kingsport, Tenn.--Holston Army Ammunition Plant (HAAP); Radford, Va.--Radford Army Ammunition Plant; Chattanooga, Tenn.--Volunteer Army Ammunition Plant (VAAP); Joliet, Ill.--Joliet Army Ammunition Plant (JAAP); and Newport, Ind.--Newport Army Ammunition Plant (NAAP). At each, the processing and operating practices were discussed with plant specialists. Available data were acquired relating to emissions sources and emissions controls. The available data were augmented by survey and test data from the U.S. Army Environmental Hygiene Agency (USAEHA), by relevant reports from Picatinny Arsenal, and from the technical reference facilities of the Defense Documentation Center. The data were assessed where

possible to project emissions source characteristics (stack height, diameter, exit gas flow rate, gas composition) to be expected when the explosives-manufacturing processes were operated at mobilization production rates. Mobilization rates themselves were not based upon information obtained from the plants. In developing the projected emissions, many extensive gaps in the existing data were identified. This led to recommendations for future work to fill the information gaps and provide much needed emissions inventory data.

Waste materials were, at the time of the plant visits, burned on open ground, or in air curtain incinerators. Enclosed burning techniques were undergoing evaluation and development at the arsenals, however. Visits were made to the Picatinny Arsenal and Tooele Army Depot to obtain additional available data for assessment of emissions from closed incineration. Considerable attention was given to assessment of the methodologies for calculation of the products of controlled combustion.

Although the emissions inventories thus developed are incomplete because of data gaps, and include elements necessarily derived from theoretical principles, one inventory (RDX) provided enough approximate information to justify a limited investigation of likely atmospheric concentrations of emitted substances at plant boundaries.

For both RDX and TNT, the literature was searched to collect data on the chemical properties and potential photochemistry, ground state chemistry, and secondary reactions of both the positively identified emissions and selected suspected emissions. Reaction rate data were compiled to the extent available. The extensive numbers of chemical reactions thus obtained have been interpreted in three ways. First, potentially hazardous compounds are identified by assessing the toxicological properties of the reactants and products. Second, the reactions themselves are screened to provide some focus on expected principal products. Third, methodologies were applied toward estimating concentrations of emitted pollutants at the boundary of a mobilized plant. Additional work on modeling the air chemistry over the plant is needed, however, and recommended.

This is Volume 4 of the final report. The study of open burning and incineration of waste munitions is covered. Other volumes are: 1--Executive Summary and General Appendices; 2--RDX/HMX production/ and 3--TNT Production.

6.C.1 OPEN BURNING AND INCINERATION OF WASTE MUNITIONS

6.C.1.1 Introduction

Problem Statement

In the interest of national security, enormous inventories of propellants, explosives, and pyrotechnics are maintained. Because the items held in the stockpile are subject to deterioration and obsolescence, leading to potential safety hazards, safe procedures for their removal have to be developed. There are a number of options presently available for disposing of waste munitions. The materials may be sold, recycled or salvaged as much as possible, and incineration technology is being developed. However, open burning still is and will continue for some time to be a method of disposal for practically all waste munitions. There are several undesirable features associated with this method. For example, it is a source of serious air pollution and a fire hazard to operating personnel, disposition is limited by weather conditions, and efficient disposal of large quantities of waste explosives is involved.

Current Status of Munitions Disposal At RAAP, VAAP, and HAAP

Open burning is practiced at three munitions plants, RAAP, VAAP, and HAAP. Of these plants, only RAAP also has an air-curtain incinerator (built in 1976) and a prototype rotary kiln incinerator (250 pounds per hour) which have been evaluated since 1972. Two full size rotary kilns (550 pounds per hour) are scheduled for completion at RAAP in 1978. The air curtain incinerator is used mainly for disposal of explosives contaminated materials: packaging, paper, rags, and other contaminated waste.

Open Burning Disposal Site Criteria

The "typical" waste munitions open burning disposal site shall meet the following requirements:¹

1. Unless otherwise specified, the disposal site shall be located at the maximum practical distance (but not less than 1,800 feet) from any inhabited building, public highway, passenger railroad, magazine, etc.

2. The open burning shall be done only on specially prepared earthen pads.
3. The terrain in the immediate vicinity of the burning pads must be approximately level and shall be cleared of all extraneous combustible material (e.g., leaves, grass, etc.) within a 200-foot radius of all burning pads.

Waste Disposal Sites Visited

A visit to the open burning site at HAAP indicated that it met all of the criteria outlined above.

The open burning site at VAAP was not visited.

At RAAP, the open burning site was not inspected, although its location was observed and a "General Site Plan" of its location was provided. Using the General Site Plan as a reference, the RAAP open burning site does not seem to meet the established site criteria. In general, the burning pads were not 1,800 feet away from some of the magazines and some of them were only 1,050 feet away from the magazines. Also, the site does not appear to be at least 1,800 feet away from inhabited buildings.

According to the General Site Plan, the burning pads do not have a 200 foot radius of cleared terrain since some of the pads are situated right next to the New River.

At RAAP, both the air curtain and the prototype rotary kiln incinerators were visited. The air curtain incinerator consists of a motor, a blower, and air manifold with a group of nozzles, and a pit. The pit was concrete lined and approximately 8 feet wide, 12 feet deep, and 20 feet long. A high air flow from the blower, typically about 100 mph, is pumped through the manifold system and distributed along with entire top edge of the longest pit dimension.

The air flow is directed as a "curtain" of air against the opposite wall of the pit and into the lower portion of the pit. The air curtain provides an increased amount of air and sets up a circular air flow in that pit that results in the combustion gases being recirculated through the burning area enabling combustible materials and primary combustion products such as particulates, CO, and hydrocarbons to burn more completely.

The rotary kiln facility consists of a conveyor arrangement for delivering the disposal material, grinder, slurry tank, piping, pump, metering equipment, rotary kiln, afterburner, pre-cooler, scrubber, and exhaust stack. The bulk explosives and propellants are ground under water to a particle size of 0.1 inch or less and then discharged into a constantly agitated vessel. The slurry consists of approximately three parts of water and one of explosives. The feed rate is 250 lbs per hour of explosives and 750 lbs per hour of water for a total slurry feed of 1,000 lbs per hour. After the water evaporates from the slurry, the explosives ignite and burn. The kiln cylinder is heated to 1600°F (871°C) by a burner using No. 2 fuel oil. The combustion products go through an oil-fired after burner to burn CO and hydrocarbons. The gases then go through a pre-cooler and a marble bed wet scrubber. The exhaust coming out of the stack is monitored for particulates and a number of other pollutants.

6.C.1.2 Open Burning

Major Types of Materials Burned

A large variety of explosives, propellants, and explosives contaminated materials are open burned every month. An attempt has been made to compile most of the more common types of explosives, explosives contaminated materials, and propellant ingredients. In Table 6C-1 are listed the major types of explosives and propellants burned. In Appendix 5 are listed common military packaging materials as potential explosives contaminated materials that may be burned. In Table 6C-2 are listed various propellant ingredients other than the major explosive components themselves. Such components need to be considered because RAAP and many Army Depots dispose routinely of high energy propellants. According to the report of Urasits, et al.,⁴ the selection of the packaging materials was made in close coordination with Natick Laboratories and the term "chemical" was used to denote materials such as lubricants, cleaning fluids, and preservatives at the expressed request of Natick Laboratories. Presumably, the selected 104 military packaging materials represent those that are most commonly used for a wide variety of packaging purposes.

TABLE 6C-1 MAJOR TYPES OF EXPLOSIVES, EXPLOSIVE COMPONENTS, AND PROPELLANTS
OPEN BURNED^{1,2,3}

Composite Explosive	Single Component
Single-base propellants (MIMIL-P-309A, M12, IMR)	TNT
Double-base propellants (Ballistite JP 204, BDI, T25, ABL)	RDX, desensitized RDX, RCA
Triple-base propellants (M17, T20, M31)	HMX
Composite modified double-base propellants	NH ₄ ClO ₄
LEW (liquid explosive wastes)	NG
Composition A-3, A-4, A-5	NC
Composition B, B-4	Nitroguanidine
Composition C-3, C-4	NH ₄ NO ₃
Composition D-2	Ba(NO ₃) ₂
Composition H-6	Dinitrotoluene
PBX 9010, N-1, N-3, 9404, Type A, Type B	Diphenylamine
Tritonal	Ethyl Centralite
HBX-1	2-Nitrodiphenylamine
Cyclotols	Potassium Nitrate
Pentolite	"White Compound"
Black Powder (Benite)	Tetryl
Smokeless Powder	PETN
Minol-2	
Octol 75/25	
High energy propellants	

TABLE 6C-2 COMMON PROPELLANT INGREDIENTS

Aluminum
Acetone
Benzene
Carbon
Cellulose
Cellulose Acetate
Cupric Salicylate
Dibutylphthalate
Diethyl Ether
Diethylphthalate
Dimethylphthalate
Di-n-propyl adipate
Dioctylphthalate
Ethyl Alcohol
Lead- β -Resorcylate
Lead-2-Ethylhexoate
Lead Salicylate
Lead Stearate
Potassium Sulfate
Resorcinol
Starch
Sulfur
Triacetin
Wood's Metal

The materials selected consist of chemicals, glasses, metals, papers, plastics, textiles, and woods. The chemical preservative and packaging compounds selected are normally used in conjunction with other forms of packaging to protect a product from abrasion, wear, or chemical corrosion. Of the 104 materials selected, 87 are solids which are the actual structural materials for solid or flexible containers, wrappings, seals, partitions, strappings, bags, printed matter, and pallets. Paper and paperboard dominate the packaging materials field and represent about 50 percent of all packaging consumed. Plastics represent a large segment and the fastest growing category of packaging materials. Plastics are used in bottles, films, coatings, pipes, pallets, and a variety of other structural products. Glass makes a strong container with high gloss and transparency. Based on total U.S. tonnage, glass represents approximately 18 percent of the total tonnage of packaging

materials. Metals provide the strongest containers available and account for approximately 16 percent of the total tonnage of packaging wastes. Wood is a traditional packaging material but represents only a minor segment of all packaging materials today--approximately 9 percent. Textiles account for about 0.5 percent of all packaging wastes. Most textile packaging is in the form of bags or sacks, which are made from either burlap or cotton. Only a small amount of synthetic fibers have been used as of yet.

Composition And/Or Chemical Structure of Materials Burned

Representative data on explosives compositions and chemical structures have been assembled in Appendix 6. The materials have been arranged into three main groups: (1) Explosives and Propellants Components, (2) Common Military Packaging Materials, and (3) Common Propellant Ingredients. The explosives and propellants components have been further subdivided into pure compounds and composite explosives. Only the materials that have been burned or would be expected to be the more common types of materials to be incinerated have been assembled.

Quantities of Materials Burned

By Plant

Army, Navy, Air Force, and Government-Owned-Contractor-Operated facilities are presently engaged in the open burning of waste explosives and explosives contaminated wastes as one of the disposal methods. The amounts of waste explosives burned by the installations we visited are tabulated in Table 6C-3 and explosives contaminated wastes in Table 6C-4.

Presumably the data on waste explosives are relatively reliable since records are maintained. The data on explosives contaminated wastes are less reliable since records on all wastes disposal by open burning are not always maintained. The general decline in all materials disposed of reflects a peacetime environment with the corresponding decreased production levels.

TABLE 6C-3 QUANTITIES OF WASTE EXPLOSIVES BURNED BY ARMY INSTALLATIONS⁵

Installation	1974	Tons per Year	
		1975	1976
Radford	1080	720	~ 600*
Volunteer	245	245	---
Holston	215	228	
Tooele	221	137	---

* Reference 2

TABLE 6C-4 QUANTITIES OF EXPLOSIVES CONTAMINATED WASTES BURNED BY ARMY INSTALLATIONS⁵

Installation	1974	Tons per Year	
		1975	1976
Radford	540	372	~ 180*
Volunteer	84	84	---
Holston	31,620	14,268	
Tooele	6	6	---

* Reference 2

By Type of Material

The types of materials burned depend very much upon the activities of the facility considered. Thus, the primary materials burned at Volunteer will consist mainly of scrap and waste produced in the manufacture of TNT.

Holston did not supply this information although materials related to the manufacture of RDX and HMX would be expected to be the primary materials burned.

Radford burns a large variety of materials. Thus, scrap and waste produced in manufacture of nitrocellulose base propellants and explosives, waste TNT and sawdust containing nitroglycerin are the primary materials. In addition to these materials, it is occasionally necessary to burn process waste and rejected material from the rocket manufacturing operations. The types of munitions materials burned by Radford may be summarized as follows:

- single-base propellants
- double-base propellants
- triple-base propellants
- high-energy propellants
- rocket casting powders
- cast and solventless rock grains
- rolled sheet propellants
- TNT.

The primary explosives involved in these mixtures are: nitrocellulose, nitroglycerin, ammonium perchlorate, ammonium nitrate, RDX, and HMX.

Army Depots such as Tooele conducting munitions deactivating handle a tremendous variety of explosives and explosives contaminated materials. This includes an extremely wide variety of explosives, organometallics, primers, fuses, and various incapacitating chemicals. Thus, it may be projected that all of the explosives and explosives contaminated materials mentioned in this report are burned by depots at one time or another.

Estimated Quantities of Materials Burned by All Army Installations

Thirty-two Army installations, located in 25 States, conducted open burning of waste explosives and explosives contaminated materials periodically during 1975.¹ The quantities of waste explosives and explosives contaminated materials open burned by these installations are shown in Table 6C-5 and 6C-6, respectively.

TABLE 6C-5 QUANTITIES OF WASTE EXPLOSIVES OPEN BURNED BY ARMY INSTALLATIONS*

INSTALLATION	TONS PER YEAR	
	1974	1975
<u>ARMY AMMUNITION PLANTS</u>		
Radford	1080.0	720.0
Iowa	498.0	518.4
Longhorn	355.2	355.2
Milan	289.2	289.2
Louisiana	252.2	165.6
Volunteer	244.8	244.8
Holston	214.8	228.0
Joliet	213.6	133.2
Lone Star	75.6	42.0
Lake City	69.6	69.6
Indiana	67.2	74.4
Kansas	46.8	46.8
Twin Cities	1.2	1.2
<u>ARSENALS</u>		
Pine Bluff	164.6	164.4
Redstone	116.4	139.2
Picatinny	63.6	63.6
Edgewood	4.8	4.8
<u>DEPOTS/DEPOT ACTIVITIES</u>		
Seneca	1312.8	816.0
Anniston	637.2	396.0
Lexington-Blue Grass	584.4	363.6
Letterkenny	582.0	361.2
Tooele	220.8	136.8
Red River	188.4	116.4
Sierra	184.8	115.2
Savanna	162.0	100.8
Navajo	74.4	45.6
Pueblo	9.6	6.0
Umatilla	2.4	1.2
Wingate	1.2	1.2
<u>OTHER</u>		
Fort Sill	230.4	230.4
TOTAL	7947.6	5950.8

* From AMCPA-E Draft Memorandum, Subj: Open Burning of Waste Munitions, of 7 January 1976.

TABLE 6C-6 QUANTITIES OF EXPLOSIVES CONTAMINATED WASTES OPEN BURNED BY ARMY INSTALLATIONS*

INSTALLATION	TONS PER YEAR	
	1974	1975
<u>ARMY AMMUNITION PLANTS</u>		
Holston	31620.0	14268.0
Kansas	1560.0	1560.0
Lone Star	1560.0	780.0
Milan	936.0	936.0
Radford	540.0	372.0
Joliet	288.0	96.0
Iowa	240.0	240.0
Badger	204.0	120.0
Sunflower	132.0	204.0
Louisiana	96.0	36.0
Indiana	96.0	180.0
Volunteer	84.0	84.0
Longhorn	48.0	48.0
Lake City	12.0	12.0
<u>ARSENALS</u>		
Pine Bluff	456.0	456.0
Picatinny	192.0	192.0
Redstone	36.0	48.0
Edgewood	24.0	24.0
<u>DEPOTS/DEPOT ACTIVITIES</u>		
Seneca	7440.0	4620.0
Savanna	1152.0	720.0
Letterkenny	900.0	564.0
Red River	336.0	204.0
Lexington-Blue Grass	288.0	180.0
Sierra	228.0	144.0
Anniston	192.0	120.0
Tooele	6.0	6.0
Umatilla	6.0	6.0
TOTAL	48,672.0	26,172.0

*From AMCPA-E Draft Memorandum, Subj: Open Burning of Waste Munitions, 7 January 1976.

Combustion Products Generated

Combustion Products Sampled

From discussions with the personnel at RAAP, HAAP, and VAAP, it became apparent that no sampling of combustion products generated in the open burning of explosives has been conducted. Attempts at locating any pertinent information on this point resulted in the discovery of some work that the Ammunition Equipment Office at Tooele had done.⁶ According to a report by Ralph W. Hayes, only minimal previous work had been conducted in the Soviet Union and in this country by the Burlington and Pantex AEC Plants.

The previous work, as well as that conducted by the Ammunition Equipment Office, has been very small scale (25 g maximum charge) and is thus open to questions as to its relevance to large scale open burning. Only the following gaseous components were sampled for:

O₂, N₂, CO, CO₂, NO_x, CH₄, HCl, HF, P₂O₅, and soot.

Burlington has conducted gas sampling tests by burning 6 g of various explosives and then extrapolating the results to a large scale open burning of 3.8 tons (the average daily amount burned) of explosives for the purposes of estimating daily pollution emissions. Some of the data are tabulated in Table 6C-7

TABLE 6C-7 ESTIMATED DAILY POLLUTION EMISSIONS FROM BURNING EXPLOSIVES

Pollutant	Burning 3.8 Tons PBX-9404	Burning 3.8 Tons LX-09	Burning 3.8 Tons Comp B-3	Burning 3.8 Tons TNT
Carbon Monoxide (lbs.)	23	4	19	213
Oxides of Nitrogen (lbs.)	144	110	141	570
Hydrocarbons (lbs.)	0	0	0	4
Phosphorous Pentoxide (lbs.)	49	0	0	0
Hydrochloric Acid (lbs.)	87	0	0	0
Hydrofluoric Acid (lbs.)	0	23	0	0
Soot (lbs.)	0	0	0	684

Mason and Hanger, Silas Mason Co., Inc., have also conducted experimental burns of several explosives to determine "typical" emission factors for the open burning of these materials.⁷ A summary of some of their results is presented in Table 6C-8. However, the burns again were made on very small quantities (of the order of one gram) of these materials. The test apparatus supposedly was designed to simulate open burning conditions. However, because of the differences in the quantities burned and the wide variety of conditions encountered in actual practice, such simulations can never be completely representative of actual open burning. Thus, any such calculations are highly tenuous at best.

Combustion Products not Sampled but Expected to be Present as Deduced From Other Work

In addition to the more prevalent air pollutants listed above, the open burning of waste explosives and propellants may result in the emission of lesser amounts of a number of other potentially harmful substances. Table 6C-9 lists some additional air pollutants which can arise from the open burning of waste explosives and propellants which may pose potential environmental and/or personal hazards.¹ Generally, these secondary substances comprise only a very minor amount of the total open burning emissions, since they arise from a small portion of the waste explosives and propellants being open burned. However, many of the emissions resulting from the open burning of pyrotechnic materials either are known or suspected to be potentially quite hazardous. Pyrotechnics account for only approximately three percent of the current Navy inventory of waste explosives and propellant materials awaiting disposal, and only a portion of these pyrotechnics are being open burned.

It is well known that polycyclic aromatic hydrocarbons may be produced during the incomplete combustion of wood, oil, petroleum, cellulose, and a large variety of hydrocarbons.^{8,9} Both the fuel/air equivalence ratio and temperature have a direct effect on the production of polycyclic aromatic hydrocarbons. High equivalence ratio or low temperature or both contribute to high polycyclic aromatic hydrocarbon production.

TABLE 6C-8 EMISSION FACTORS FOR THE OPEN BURNING OF SOME EXPLOSIVES (LBS. OF POLLUTION PER TON OF EXPLOSIVE OPEN BURNED)

Explosive	Carbon Monoxide	Oxides of Nitrogen (NO _x)	Fluorocarbons & Hydrocarbons	Phosphorus Pentoxide	Hydrochloric Acid	Hydrofluoric Acid	Soot
TNT	56.0	150.0	1.1	0	0	0	180.0
Comp B-3	5.0	37.1	0	0	0	0	0
PBX 9404	6.1	37.9	0	4.0	22.9	0	0
LX-07	1.3	27.9	4.0	0	0	54.0	0
LX-09	1.1	27.9	0	0	0	6.1	0

TABLE 6C-9 SECONDARY AIR POLLUTANTS WHICH MAY RESULT FROM THE OPEN BURNING OF WASTE MUNITIONS^a

Name of Chemical Element or Compound	Present in (Some)	Potentially Hazardous Emission Products From Open Burning ^b
Aromatic Dyes	Colored smoke - producing pyrotechnics	Dyes & decomposition products
Asbestos	Pyrotechnics	Asbestos
Barium	Pyrotechnics	BaO
Boron	Liquid propellants	Decomposition Products, B ₂ O ₃
Bromine	Pyrotechnics	HBr, Br ₂
Chlorine	Pyrotechnics, propellants	HCL, Cl ₂ , COCl ₂
Chromium	Pyrotechnics, decay elements	Cr ₂ O ₃
Copper	Pyrotechnics, propellants	CuO
Fluorine	Propellants	HF
Lead	Propellants	PbO
Phosphorus (white)	Pyrotechnics (tracers & incendiaries) & ordance	P ₂ O ₅
Phosphorus (red)	Pyrotechnics	P ₂ O ₅
Selenium	Delay elements	SeO ₂
Strontium	Pyrotechnics	SrO
Sulfur	Explosives, pyrotechnics	SO ₂ , SO ₃
Trinitrotoluene	Explosives	HCN

^aEffluents which are expected to be emitted only in limited quantities.

^bEmissions may be from airborne (vaporized, aerosolized, etc.) uncombusted materials as well as partially or completely combusted materials. Emissions listed are not all inclusive.

The U. S. Public Health Service, Division of Air Pollution, has undertaken a program of field sampling to obtain measurements of pollutant emission levels from a wide variety of sources.¹⁰ Thus, under this source-sampling program, emissions to the atmosphere from many combustion processes, including open burning, are available. Of the many studies available only two will be reviewed here. One study examined the smoke plumes from the open burning sources with four different types of predominant fuel: 1) municipal refuse, 2) automobile tires, 3) grass clippings, leaves, and branches, and 4) automobile bodies.¹⁰ In addition to obtaining overall emission data, a primary objective of the study was to establish the relative importance of various combustion processes as contributors to polycyclic aromatic hydrocarbon formation. Data on polycyclic aromatic hydrocarbon formation in different open burning sources are summarized in Table 6C-10. The sampling point in each case was in the "middle" of the smoke plume.

Particulate matter collected from the open burning sources contained a higher percentage of organic material than that produced by any of the enclosed-burning sources sampled. The benzene soluble content was 65 percent for municipal refuse, 73 percent for grass and hedge clippings, 15 percent for rubber tires, and 48 percent for automobile bodies. In summary, open burning (of different fuels) generated particulate matter containing from 11 to 1100 micrograms of benzo(a)pyrene (a known carcinogen) per gram of particulate matter collected. The structures and some of the properties of the detected polycyclic aromatic hydrocarbons are listed in Table 6C-11.

The other study reviewed here was a cooperative effort between the Public Health Service and the Air Pollution Research Center of the University of California at Riverside.¹¹ It was conducted on simulated open burning of various materials (municipal refuse, landscape refuse, and automobile components). The significant differences of this study from the previous one were in the amount of material burned (100-125 lbs) and the method of collection of the generated combustion products (a large sheet metal, inverted funnel was used about 4 ft above the burning material). Samples were taken to determine the amount of particulates, CO₂, CO, gaseous hydrocarbons, NO_x, formaldehyde, organic acids, and polycyclic aromatic hydrocarbons. The data are in Tables 6C-12 and 6C-13.

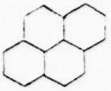


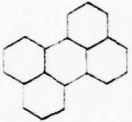


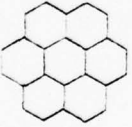

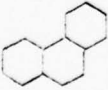
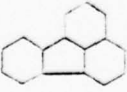

TABLE 6C-10 POLYCYCLIC HYDROCARBON CONTENT OF PARTICULATE MATTER EMITTED IN OPEN BURNING

Type of Unit	MICROGRAMS PER GRAM OF PARTICULATE										
	GROUP 1					GROUP 2					
	Benzo(a)-pyrene	Pyrene	Benzo(e)-pyrene	Perylene	Benzo(ghi)-perylene	Anthanthrene	Coronene	Anthracene	Phenanthrene	Fluoranthene	Benz(a)-anthracene
Municipal refuse	11	20	4.5	---	---	---	---	4.7	---	13	---
Automobile refuse	1100	1300	450	72	660	53	81	110	450	470	560
Grass clippings, leaves, branches	35	120	21	---	5.4	---	---	4.7	---	110	25
Automobile bodies	270	670	120	33	150	12	15	220	160	450	40

Group 1 - analytical data reliable

Group 2 - analytical data less reliable

TABLE 6C-11 PROPERTIES OF POLYCYCLIC AROMATIC HYDROCARBONS

Compound	Empirical Formula	Structure	Molecular Weight	Melting Point, °C	Boiling Point, °C	Biological Activity*
GROUP 1						
Pyrene	C ₁₅ H ₁₀		202	150	≈360	...
Benzo(a)pyrene	C ₂₀ H ₁₂		252	178	≈500	+++
Benzo(e)pyrene	C ₂₀ H ₁₂		252	178	≈500	+
Perylene	C ₂₀ H ₁₂		252	275	≈500	...
Benzo(ghi)perylene	C ₂₂ H ₁₂		276	273		...
Anthanthrene	C ₂₂ H ₁₂		276	257		...
Coronene	C ₂₄ H ₁₂		300	435	≈600	...
GROUP 2						
Anthracene	C ₁₄ H ₁₀		178	217	340	Not reported
Phenanthrene	C ₁₄ H ₁₀		178	101	340	Not reported
Fluoranthene	C ₁₆ H ₁₀		202	110	393	...
Benz(a)anthracene	C ₁₈ H ₁₂		228	160	Sublimes	-

*Relative activity of mouse epidermis: Code: +++ active, ++ moderate, + weak, ... inactive. Symposium on the Analysis of Carcinogenic Air Pollutants. Hoffman, D. and E. L. Wynder, Analytical and Biological Studies on Gasoline Engine Exhaust, National Cancer Institute, Monograph No. 9, August 1962.

TABLE 6C-12 GASEOUS EMISSIONS FROM OPEN BURNING

Gaseous Emissions--Pounds per Ton of Material Initially Present*							
Material Burned	CO ₂	CO	HC ^a	Formaldehyde	Organic Acids ^b	NO _x	Particulates
Municipal Refuse	1230	85	30	0.095	15	11	16
Landscape Refuse	700	65	30	0.006	13	3	17
Automobile Components	1500	125	30	0.030	16	8	100

* Average values

^a Gaseous-hydrocarbons expressed as methane

^b Organic acids expressed as acetic acid

TABLE 6C-13 POLYNUCLEAR HYDROCARBON EMISSIONS FROM OPEN BURNING, GRAMS PER TON OF MATERIAL INITIALLY PRESENT

	Municipal Refuse		Landscape Refuse		Automobile Components
	1	2	3	4	5
Anthracene	--- ^a	---	---	---	1.9
Phenanthrene	---	---	---	---	13.2
Fluoranthene	0.78	1.19	0.77	0.64	33.4
Pyrene	0.89	1.28	1.31	0.87	45.9
Chrysene	0.25	0.34	1.01	0.42	14.5
Benz(a)anthracene	0.17	0.21	0.26	---	19.4
Benzo(a)pyrene	0.19	0.22	0.31	0.13	17.8
Benzo(e)pyrene	0.13	0.16	0.12	0.08	9.0
Perylene	---	---	0.05	---	1.6
Benzo(ghi)perylene	---	0.19	0.21	---	12.2
Anthanthrene	---	---	0.03	---	1.4
Coronene	---	---	---	---	1.5

^a Indicates that the compound was not detected.

Limited analysis of the collected gaseous hydrocarbons on a gas chromatograph indicated 30-40 percent of the compounds to be unsaturated. In open burning, temperatures are usually fairly low and the high-intensity burning necessary for the oxidation of atmospheric nitrogen may not exist. Particulate emissions were high and when compared with corresponding incineration runs were 25 or more times higher. Another result of poor combustion conditions is the high concentration of polycyclic aromatic hydrocarbon formation. For burning auto components, the benzopyrene concentration reached 27 g/ton, which exceeds the high emissions of 12 g/ton found for a coal burning hand-fired furnace.¹²

As depicted in the photograph of the open burning of explosives and propellants (Figure 6.C-1) such processes are not very soot free.³

Ringelmann readings have been made at the burning area at the Pantex AEC Plant on wet explosives, contaminated high explosive waste, dry high explosives, and contaminated scrap metal during burning and flashing.¹³ The observation distance was 520 ft and typical results of dry high explosives burning are represented in Table 6C-14. The observations showed that the burns for all cases exceeded the desirable limit for opacity of Ringelmann No. 1 (20 percent opacity) and the burning of dry high explosives (Table 6C-14) was the "cleanest" burn. In some of the other types of burns, Ringelmann No. 4 readings existed for durations of up to 18 minutes.¹⁴ The composition of this plume will depend upon a number of factors, especially the types of wastes being burned. An open burning involving such a large plume would also probably result in appreciable amounts of uncombusted or partially combusted explosive materials being rendered airborne by such means as vaporization, aerosolization, etc.

Thus, the implications of the other open burning test results are that significant concentrations of carcinogenic materials may also be generated in explosives and propellant burning.



Figure 6.C-1 Open Burning Site

TABLE 6C-14 BURNING OF DRY HIGH EXPLOSIVES

Time in Seconds	Ringelmann No.	Opacity %
15	0	0
30	0	0
45	3	60
1 minute	4	80
75	4	80
90	4	80
105	4	80
2 minutes	4	80
135	4	80
150	4	80
165	4	80
3 minutes	4	80
195	4	80
210	4	80
226	4	80
4 minutes	4	80
255	4	80
270	4	80
285	4	80
5 minutes	3	60
5'15	3	60
5'30'	3	60
5'45'	2	40
6'	2	40
7	1	20
8	0	0

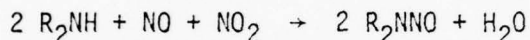
Combustion Products Not Sampled But Probably Present as Deduced from Relevant Chemistry

Nitrosamines --

The environmental distribution of N-nitroso compounds has been placed in a new perspective since N-nitrosodimethylamine (DMN) was found in the air in two U. S. cities.^{15,16} Using a new sensitive and selective detection system for N-nitroso compounds,¹⁷⁻¹⁹ Fine, et al. found DMN at the 3.0 to 320 ng/m³ level in the air in Baltimore, Maryland at the 5.0 to 170 ng/m³ level in the air in Belle, West Virginia. DMN has also been reported in

nearby Curtis Bay and in the Kanawha River in Belle.²⁰ Because N-nitrosamines have been absent in aquatic and atmospheric environments, the possibility that a compound as carcinogenic as DMN may be an air pollutant had not been previously considered.

The chemical formation of nitrosamines has been the subject of numerous studies that have recently been reviewed by Mirvish.²¹ Although most of the reported studies have been concerned with condensed-phase reaction systems, the formation of nitrosamine in the gas phase has been demonstrated.^{22,23} Neurath *et al.*²³ showed that the formation of nitrosamines from secondary amines requires an equimolar mixture of nitrogen oxides. This reaction, which occurs in the gaseous phase, can be represented as follows:



Bretschneider and Matz²² showed that diethylamine and nitrogen dioxide (NO_2) at concentrations of 50 to 100 parts per million (ppm) reacted within seconds to form measurable levels of nitrosamine.

Some work with gas-phase systems is currently being conducted by EPA.²⁴ In this study, gaseous dimethylamine, $(CH_3)_2NH$, has been shown to react with gaseous nitrous acid, $HONO$, in air to yield N-nitrosodimethylamine, $(CH_3)_2N-NO$. This on-going research has shown that, in a humid atmosphere containing dimethylamine, NO , NO_2 , and $HONO$ at concentrations of 0.5 to 2 ppm, the amine reacted at a rate of about 4 percent per minute yielding N-nitrosodimethylamine as the major reaction product. In the absence of $HONO$ and humidity, the rate was lower by a factor of four, approximately. It now appears that a much more intense look will have to be taken at the concentrations of nitrosamine precursors in pollutant atmospheres. Thus, knowledge of the environmental concentrations of nitric oxide, nitrogen dioxide, nitrous acid, nitrites, nitrates, and primary, secondary, tertiary, and quaternary amines will be required.

The nitric acid manufacturing area at HAAP had a very high ambient NO_x concentration. Just east of this area, in the path of prevailing winds, is the "B Line" area. In this area, ammonia along with other low molecular weight amines is recovered from the spent acetic acid. Thus all ingredients for ambient nitrosamine formation appear to be present in this locale and their formation should be investigated.

Carbonyl Sulfide --

Even though SO_3 is the more stable species at ambient conditions, SO_2 is the predominant species formed because the gas phase reaction between SO_2 and O_2 is too slow to produce much SO_3 . It has been reported that the reaction of sulfur dioxide with carbon monoxide results in the formation of not only carbon dioxide and sulfur but also carbonyl sulfide.²⁵ The lowest published lethal concentration of carbonyl sulfide in air by inhalation in mice is 2900 ppm as compared to 2000 ppm for carbon monoxide.²⁶ Thus, carbonyl sulfide, although not necessarily specific to only AAP's, is another species to be investigated especially under substoichiometric oxygen combustion conditions that exist in open burning.

6.C.1.3 INCINERATION

Status as of 1977

Incineration effort of explosives and explosives contaminated materials as of this date is still minimal. For example, of the three AAP's (HAAP, RAAP, and VAAP) of primary interest to this study, only RAAP has conducted pilot-scale incinerations with a rotary kiln incinerator since about 1972 and expects to have two full size (550 lbs/hr each) incinerators operational sometime in 1978. HAAP and VAAP did not mention installing incinerators in the near future. Of the other installations visited, Picatinny Arsenal is experimenting on a pilot-scale fluidized bed incinerator, JAAP is using a multiple chamber incinerator and Tooele Army Depot has developed and used SITPA II since about 1975. The use of the rotary furnace incinerators with minimal or no pollution abatement devices is more widespread as presumably the Army is using 20, the Navy 6, and the Air Force 2.¹ RAAP is also using and air curtain incinerator (since 1976).

Principles of Combustion

To better appreciate the various methods of incineration, a brief description of the various types of incinerators used will be given first. All incinerators are designed around the three "T's" of combustion: time, temperature, and turbulence. The volume of the chamber should be large enough to contain the gas flow a sufficient time for the complete combustion of the solid (liquid) waste and gaseous degradation products. Heat is used as the driving force to sustain combustion, and thus temperature is one of the most important factors in combustion to affect complete combustion of difficult to burn materials as well as combustion of various gaseous components (odor, smoke). Turbulence is important to provide for thorough mixing of the products of combustion with the air (oxygen) necessary for complete combustion.

The air requirements differ for different types of waste combusted because of their different BTU values. Air may be introduced in the incinerator by natural draft through a chimney or stack. The higher the stack, the greater the amount of air that can be brought into the incinerator. Other ways of introducing air are with fans that blow air into the incinerator, forced draft, or pull air through the incinerator, induced draft. Excess air is usually introduced for two reasons: (1) to insure complete combustion, and (2) to regulate incinerator temperature.

Types of Incinerators

A large number of incinerators have been or are being investigated for the disposal of waste explosives and explosives contaminated materials. A list of the various incinerators along with the evaluating organizations is given in Table 6C-15.¹ The conclusions of these investigations along with an illustration of each type of incinerator are presented below.

TABLE 6C-15 TYPES OF INCINERATORS

Incinerator	Evaluating Organization
Air Curtain	DuPont; RAAP
Closed Pit	ERDA-PANTEX
Batch Box	Navy Ammunition Production Engineering Center (NAPEC)
Rotary Demil Furnace	Tooele Army Depot; NAPEC
Rotary Kiln	RAAP
Fluidized Bed	Exxon Research & Development; Picatinny Arsenal
Wet Air Oxidation	Naval Ordnance Station (NOS)
Molten Salt (Fused Salt)	NAVORD; Rockwell International
SITPA I	Tooele Army Depot
SITPA II	Tooele Army Depot
Vortex Incinerator	RAAP
Vertical Induced Draft	Picatinny Arsenal
Multiple Chamber	JAAP

Air Curtain^{34,35}

A schematic of the air curtain is given in Figure 6.C-2. The Air Curtain Incinerator (ACI) concept was initiated by E. S. Moore, Jr., of E.I. DuPont de Nemours Co., in 1964. RAAP has been using one since 1976. DuPont used ACI for disposal of nitrocellulose and dunnage; RAAP has been using it for disposal of explosives contaminated dunnage. Temperatures as high as 1370°C (2500°F) have been measured for fires burning wood.

The potential for pollution abatement of gaseous or aerosol pollutants is small. Continuous operation is the best mode for minimum environmental effects; consequently, ACI may not be best suited for disposal of small quantities of explosives contaminated materials. Self-sustained combustion of explosive materials may require larger amounts of materials and that may pose serious safety problems. Sustaining combustion of certain fast burning explosives may not be possible.

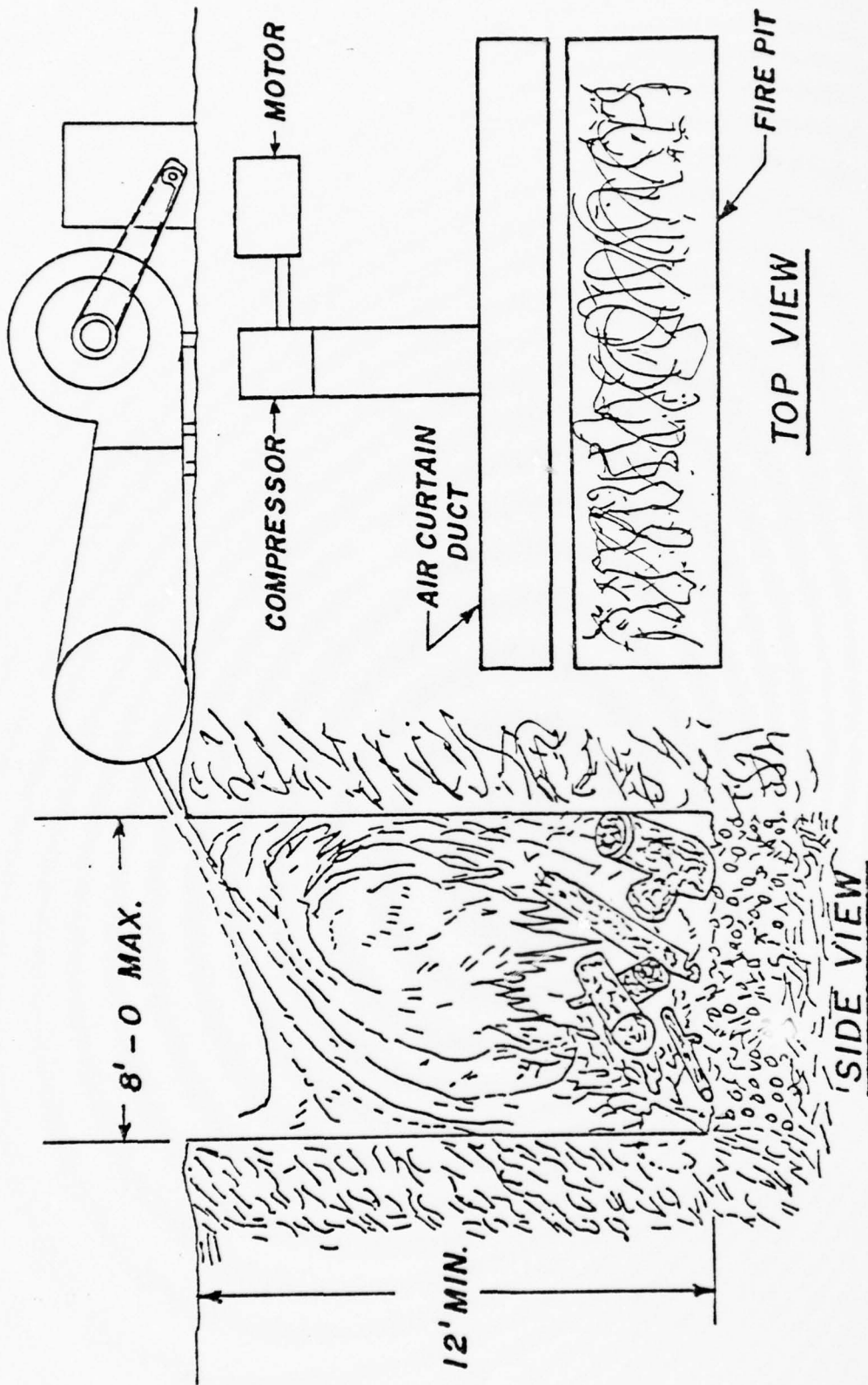


Figure 6.C-2 Air Curtain Incinerator

Closed Pit³⁶

Closed pit, batch-type incinerator is depicted in Figure 6.C-3. One of the main advantages of this type of incinerator is the low initial and maintenance costs. Also, no auxiliary fuel and no skilled operating personnel are required. Possible problems may arise in the formation of holes or channeling in the filter and the eventual disposal of the contaminated filter material.

Batch Box^{1,37}

A schematic of the batch box is given in Figure 6.C-4. The batch box incinerator is under development by the Navy Ammunition Production Engineering Center (NAPEC) for use in the disposal of small arms ammunition up to 0.50 caliber as well as explosives contaminated dunnage. Some pollution control is achieved by the afterburner and marble bed scrubber. The disadvantages-- wall erosion, water pollution, required cool down period, not amenable to continuous operation, method not suitable for large quantities of bulk explosives--are seen as quite serious.

Rotary Furnace³⁸

A schematic of the rotary furnace is given in Figure 6.C-5. A considerable amount of experience has been obtained with this incinerator at numerous Army and Navy installations. The equipment is relatively simple with a potential for controlled pollution abatement. The incinerator can be operated on a continuous or semi-continuous basis and a wide variety of explosives can be handled. A possible disadvantage may be in the erosion of the furnace walls where detonations occur.

Rotary Kiln³

A rotary kiln is depicted in Figure 6.C-6. The application of a rotary kiln for explosives disposal was investigated extensively on a pilot plant scale (250 lbs/hr) by RAAP. As a result of these investigations, two full size kilns (550 lbs/hr) are being installed at RAAP now. The distinction between a rotary furnace and a rotary kiln is on the basis of the internal construction. A rotary kiln has an internal lining of fire brick and no internal flights whereas a rotary furnace has no internal lining and has internal flights

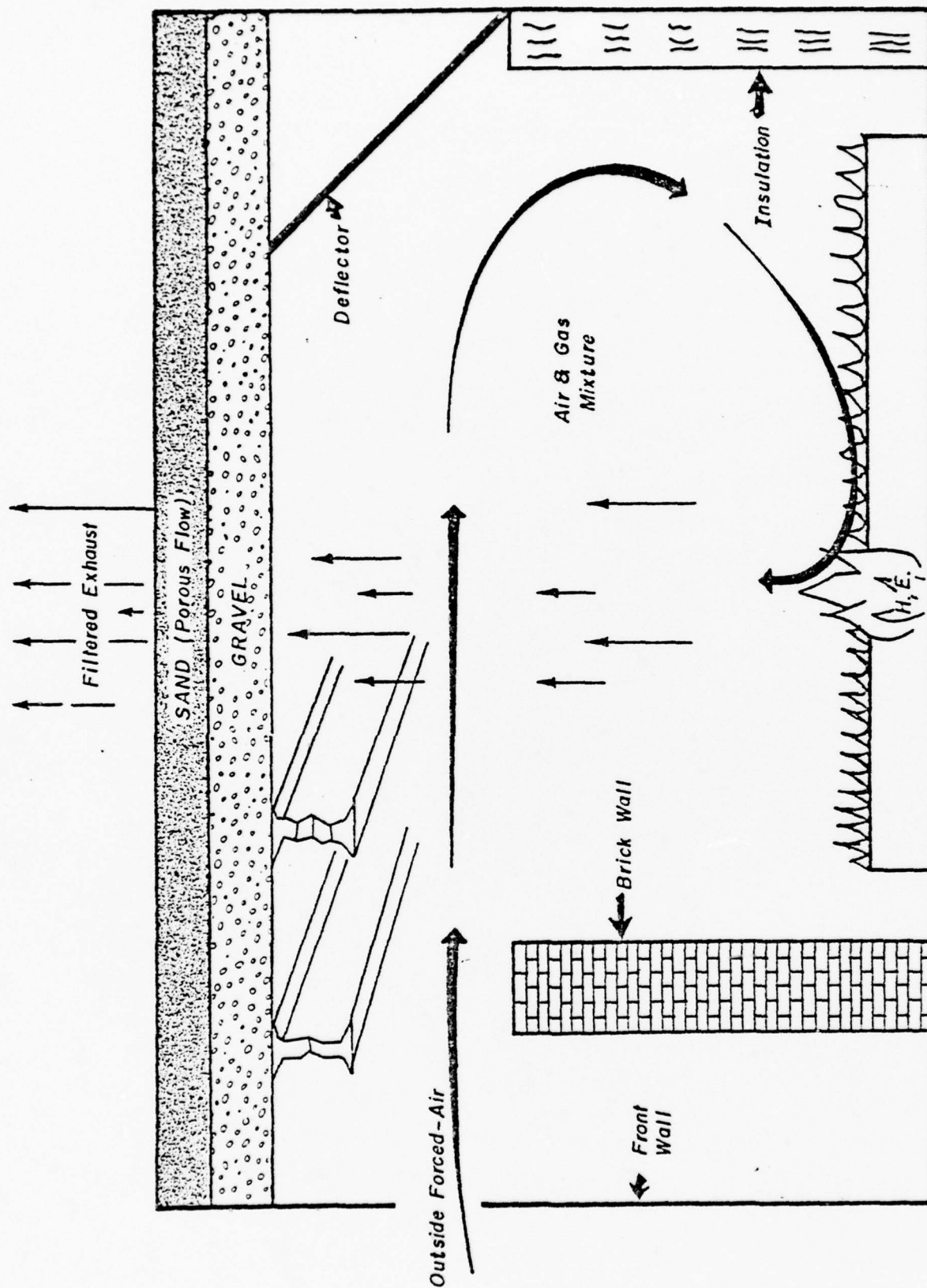


Figure 6.C-3 Closed-Pit, Batch-Type Incinerator Concept³⁶

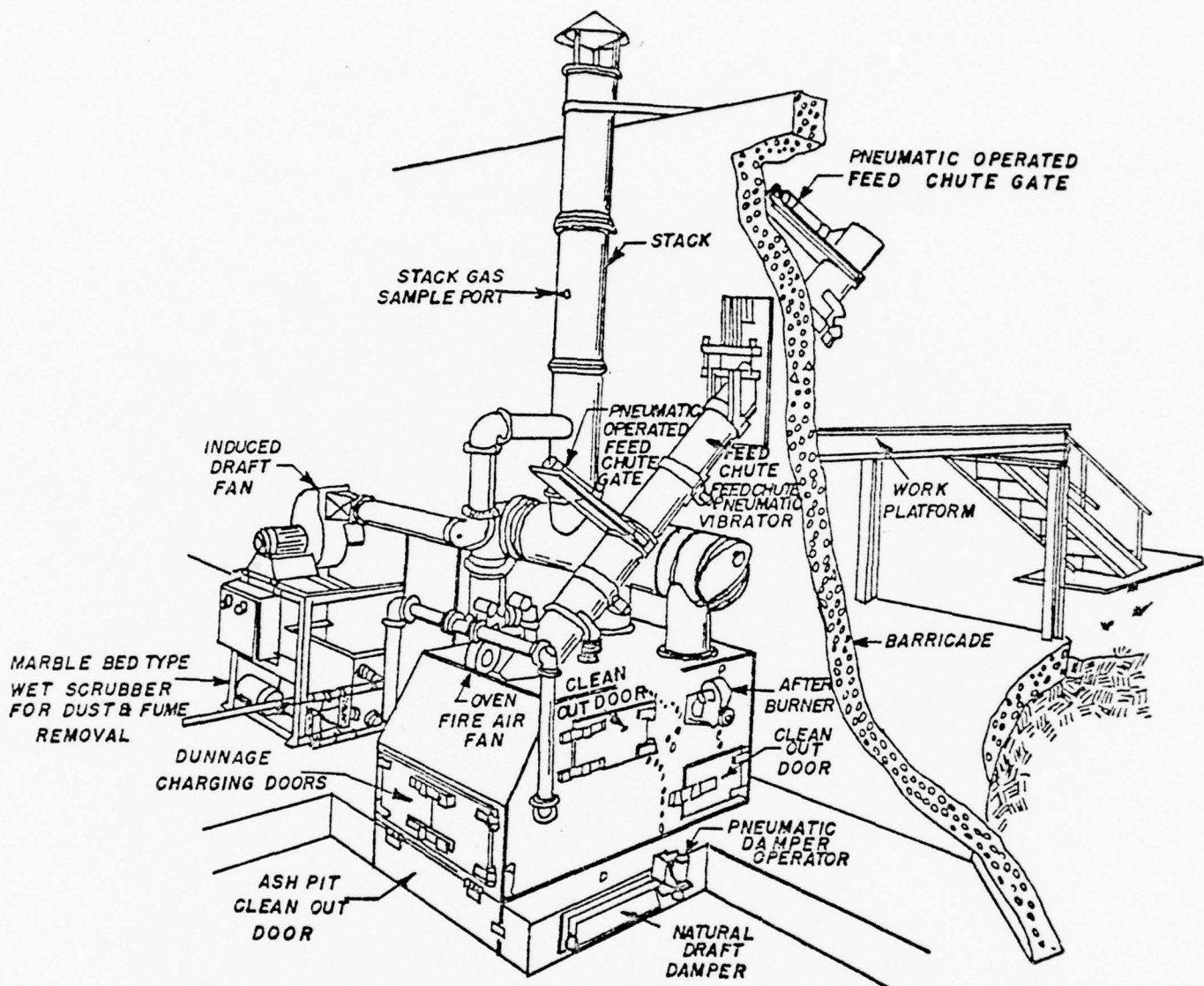


Figure 6.C-4 Batch Box Incinerator³⁷

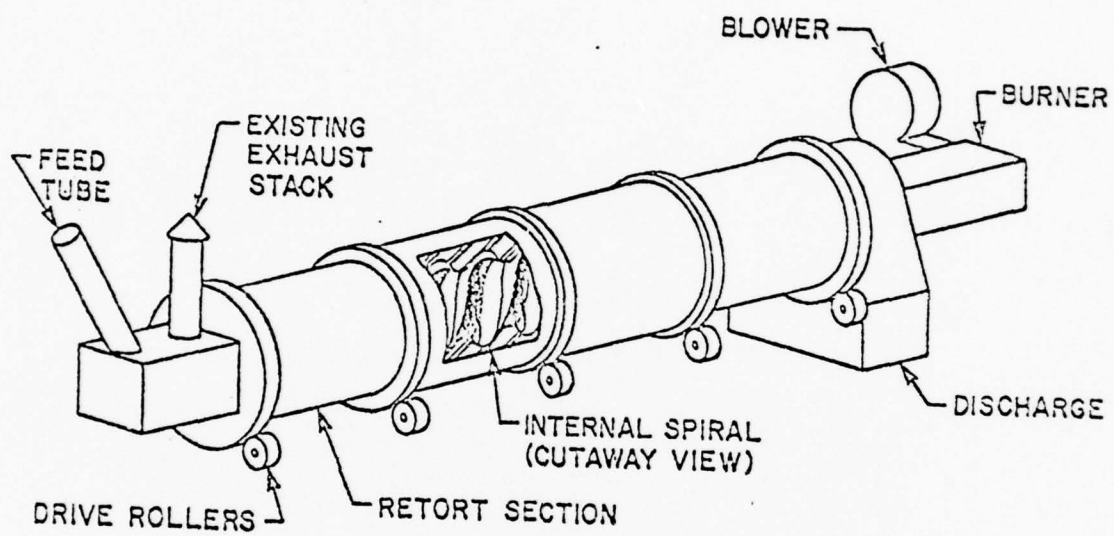


Figure 6.C-5 Rotary Demil Furnace System³⁸

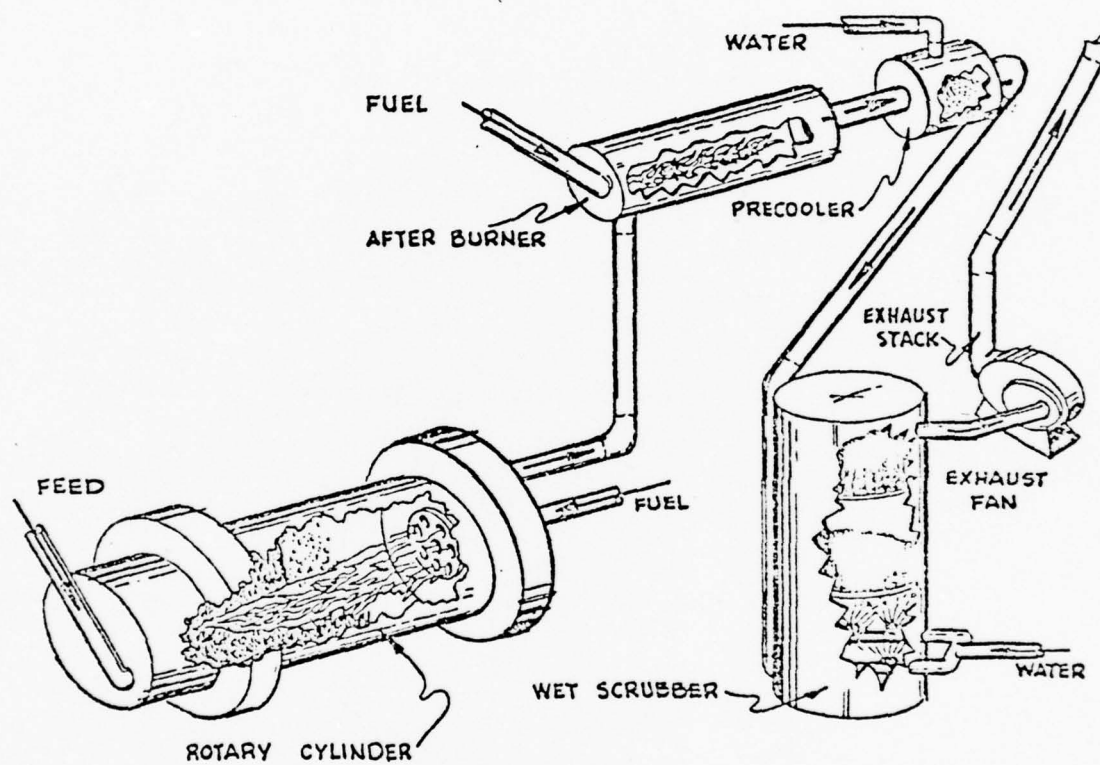


Figure 6.C-6 Rotary Kiln³

for advancing the items down the length of the furnace and for stopping propagation of detonation within the furnace. The advantages and disadvantages applicable to rotary furnaces apply also to the rotary kiln. An added disadvantage of the rotary kiln is that it uses water slurry for incineration. As the rotary kiln incinerator, developed by RAAP, has a complete pollution abatement system, its further comparison with a rotary furnace cannot be made. Therefore, more properly, rotary kilns should be compared with the SITPA II.

Fluidized Bed³⁹⁻⁴¹

A fluidized bed system is illustrated in Figure 6.C-7. This approach to incineration also uses aqueous slurries of explosive materials. The lab- and pilot-scale work has looked quite promising. The discovery and use of a nickel based catalyst in the incinerator reduced the NO_x concentration to less than 50 ppm. The system has some serious drawbacks, however. It is complex and requires skilled operators. It is expensive to build and maintain and the catalyst lifetimes are not known. Bed agglomeration from certain components (for example, CaCl_2) in various munitions is a real possibility.

Wet Air Oxidation^{42,43}

The wet air oxidation process is illustrated in Figure 6.C-8. The Naval Ordnance Station, Indian Head, MD has been investigating this process for 5 years. The lab- and pilot-scale continuous feed tests have looked quite promising. The process is a controlled-temperature process and presumably works on all kinds of aqueous slurries otherwise difficult to incinerate. It is claimed to eliminate all air pollution including NO_x . The serious drawbacks are--extremely complex equipment requiring highly skilled personnel to operate, it is a high pressure process, and because of the corrosive nature of the materials handled, requires very expensive metals for construction. There may be a water pollution problem.

Molten Salt^{44,45}

The molten salt process is illustrated in Figure 6.C-9. A bench-scale feasibility study has been conducted by Atomics International in 1973 and 1974 under contract to NAVORD. Presumably, a variety of explosives can be

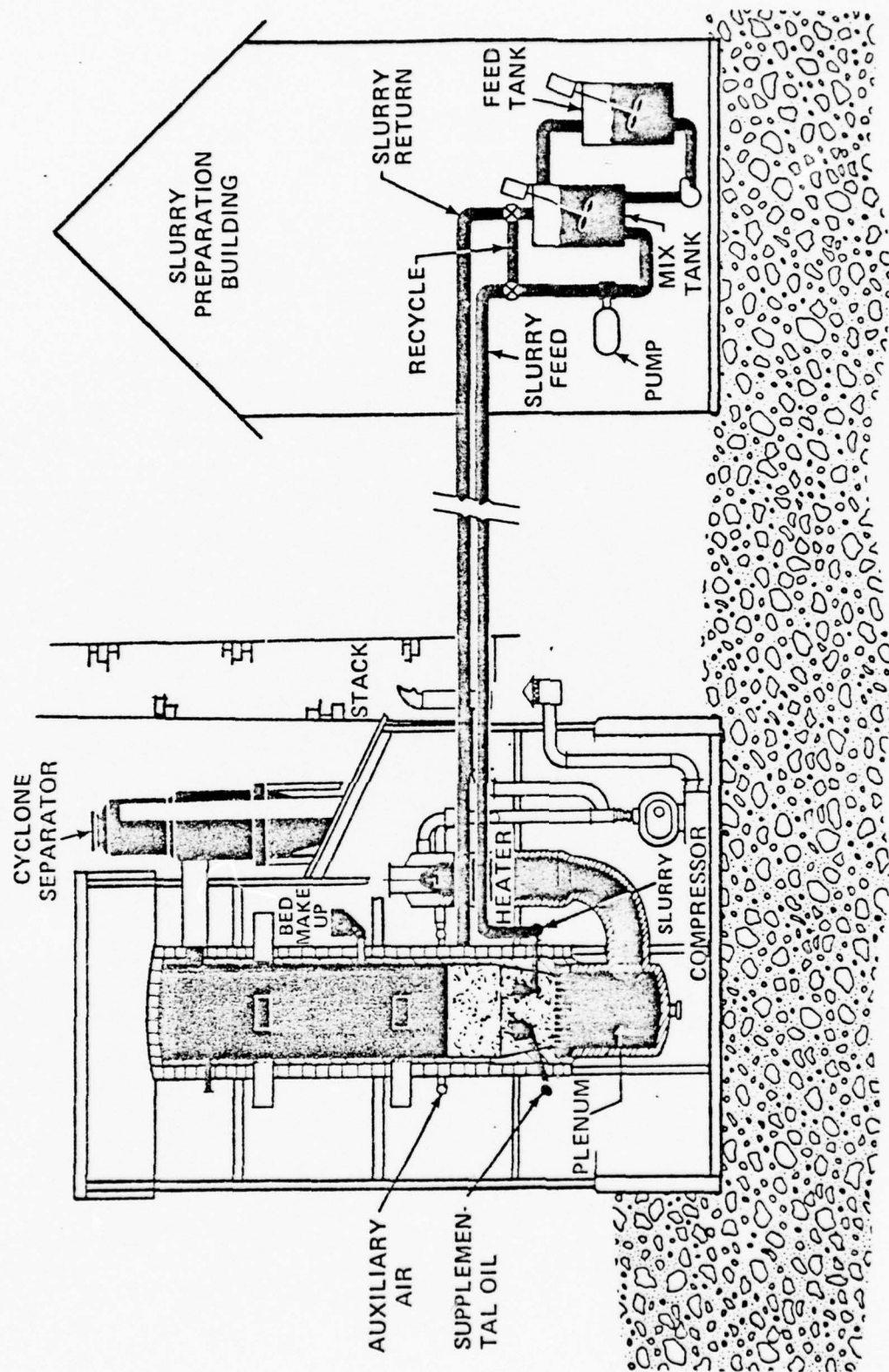


Figure 6.C-7 Fluidized Bed³⁹

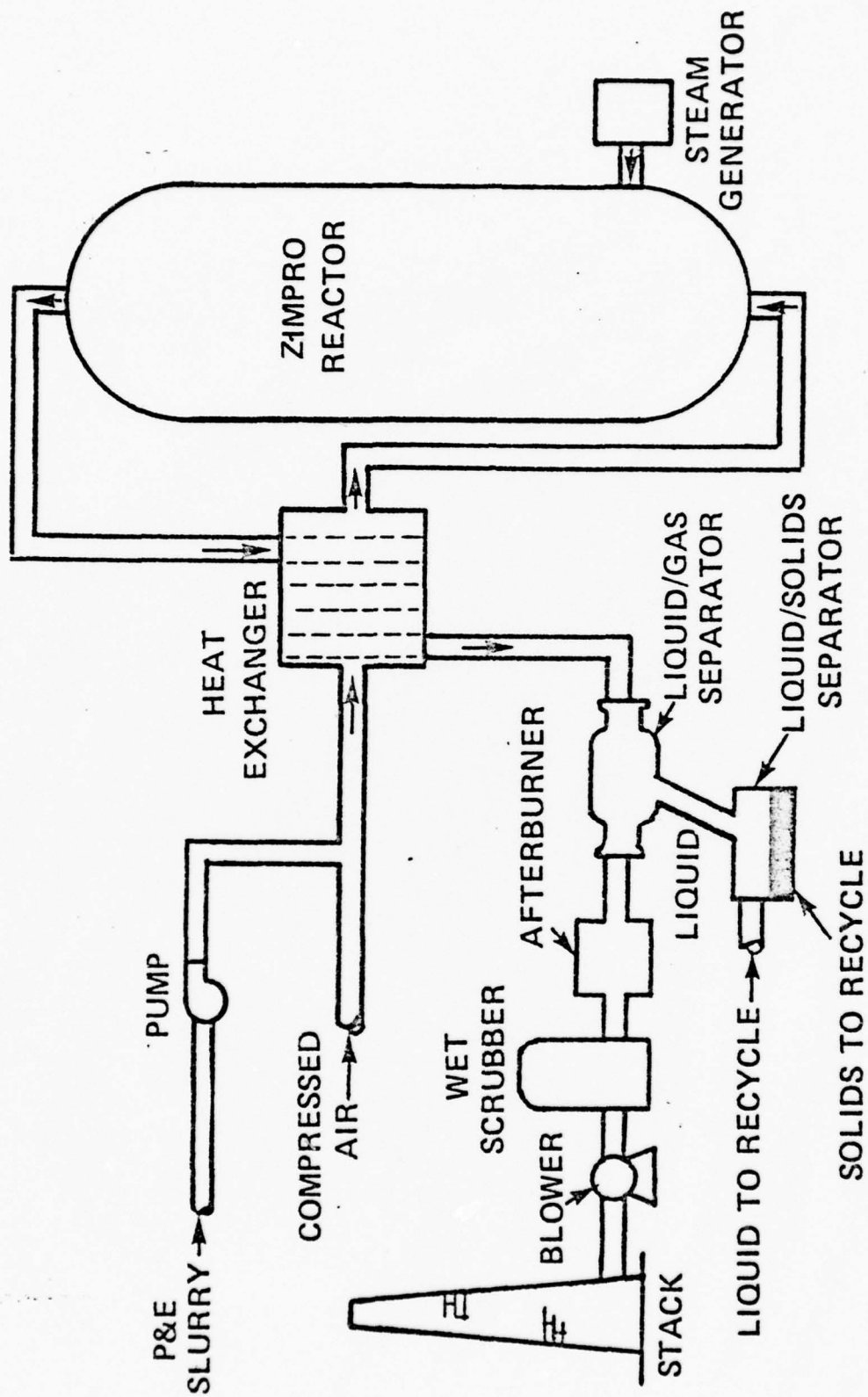


Figure 6.C-8 Wet Air Oxidation⁴²

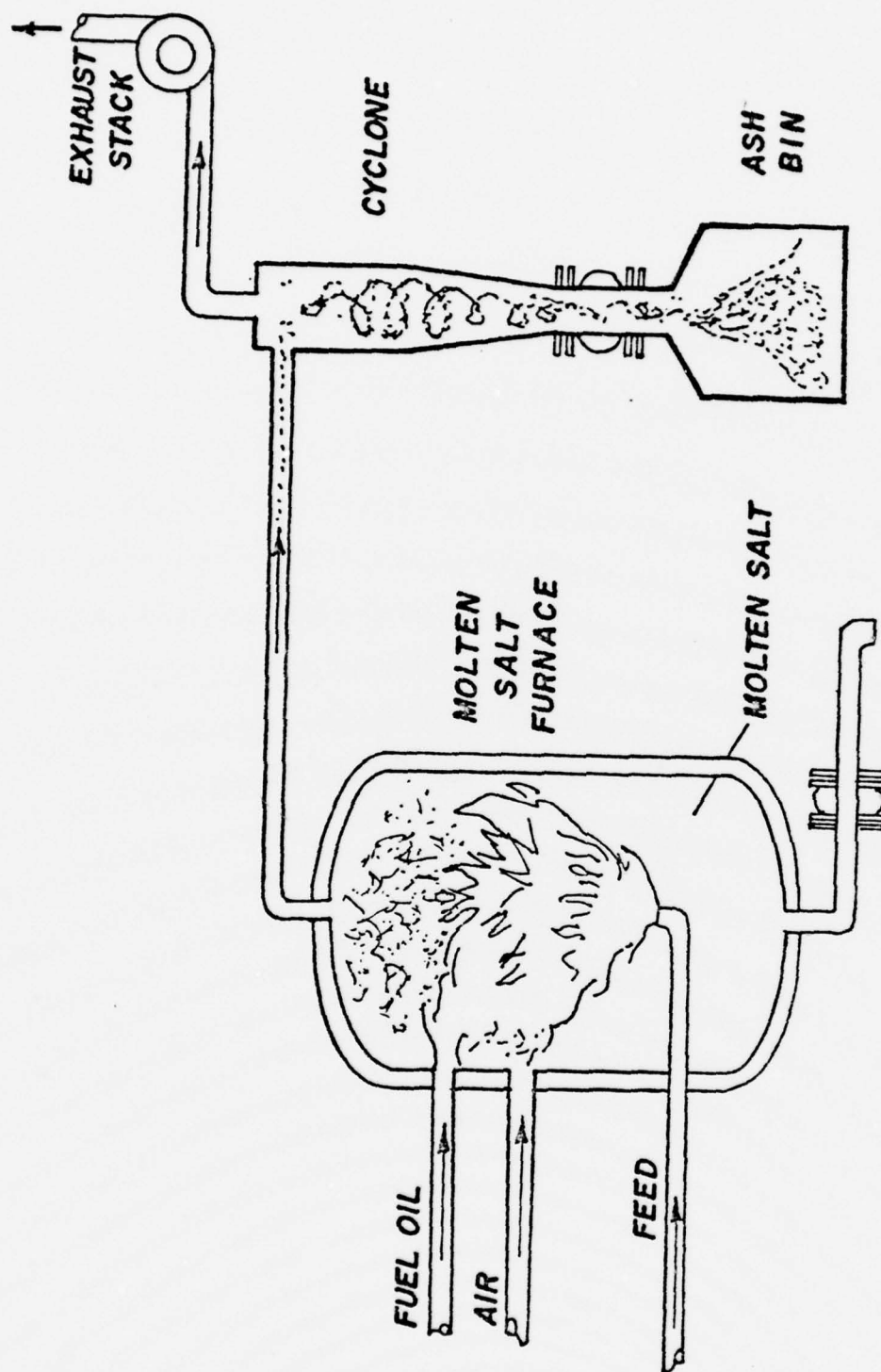


Figure 6,C-9 Molten Salt Incinerator⁴⁴

handled and a continuous operation is feasible. A potential for minimal air pollution exists. The serious drawbacks are the corrosive nature of the reaction medium, the high costs of construction and operation, and potential for explosive reactions.

SITPA I⁴⁶

One configuration of SITPA I is illustrated in Figure 6.C-10. This system has been evaluated by the Ammunition Equipment Office, Tooele Army Depot, and was found to do the job after certain modifications (mainly in the configuration of the burning pit). The process involves low initial and operating costs, is simple to operate, and is amenable to a variety of bulk explosives burning. A disadvantage is that it is a batch operation.

SITPA II^{47,48}

The three variations and a baghouse detail of a SITPA II process, available at Tooele Army Depot, are depicted in Figures 6.C-11 through 6.C-14. In essence, SITPA II consists of a Rotary Demil Furnace and a positive feed injection system plus a cyclone particulate collector, a baghouse filter, and a wet scrubber as an option. The favorable pollution abatement results, the semi-continuous mode of operation, the simplicity of operation, and low maintenance costs all favor this approach as the long range solution to explosives disposal.

Vortex Incinerator^{39,49}

A Vortex Incinerator is shown in Figure 6.C-15. In the initial screening of incineration techniques and incinerators, RAAP also evaluated the vortex incinerator. The results turned out to be unsatisfactory due to settling out of solids in the combustion chamber prior to complete combustion of the solids. Application of a vortex incinerator would seem to be limited only to certain types of liquid wastes.

Vertical Induced Draft³⁹

A schematic of this incinerator is shown in Figure 6.C-16. Picatinny Arsenal did the initial evaluation of this type and found that it was considerably less efficient than, for example, the rotary kiln or furnace. Presumably this concept is not used today in the destruction of explosives.

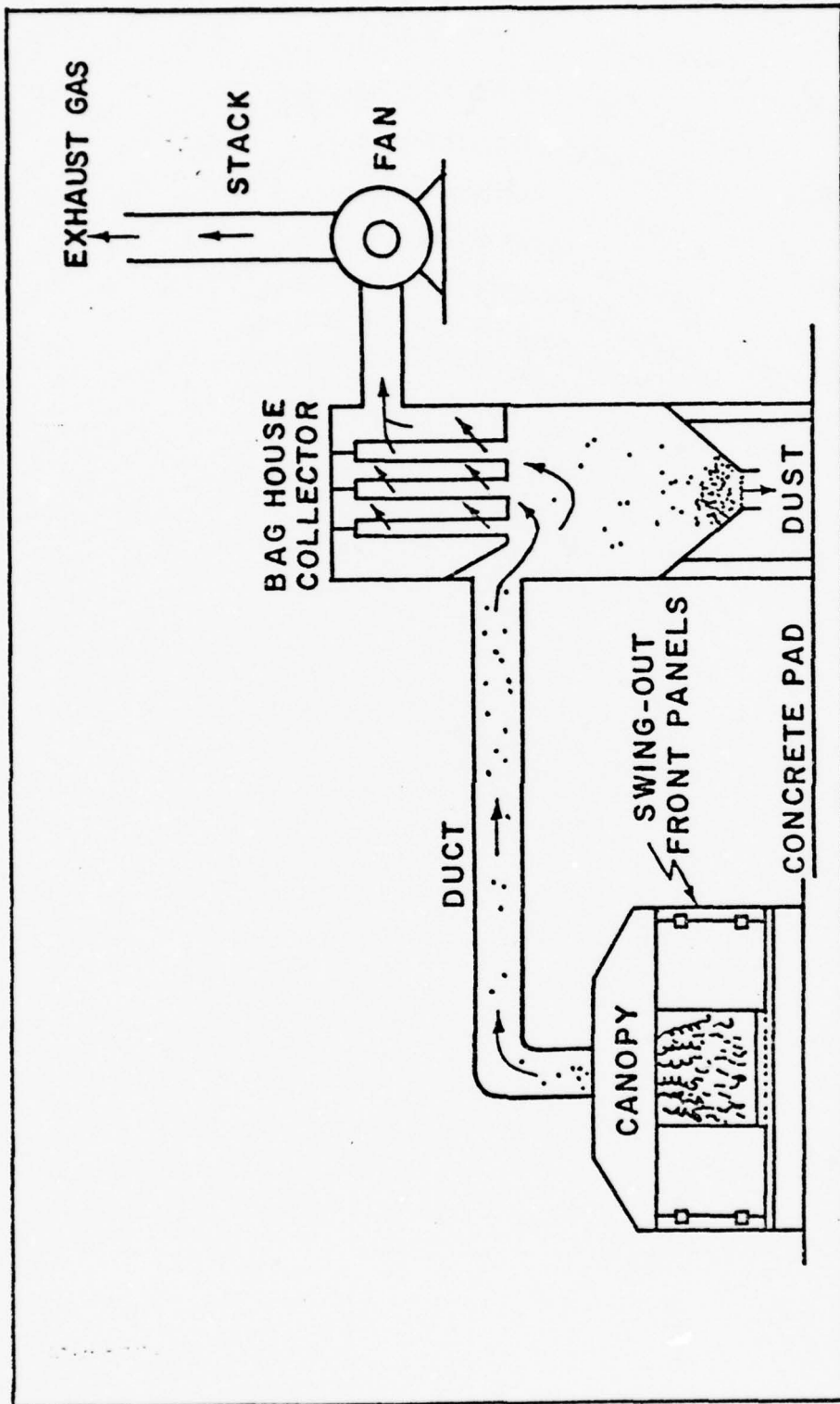


Figure 6.C-10 SITPA (Simplified Incinerator Technique for Pollution Abatement);⁴⁶

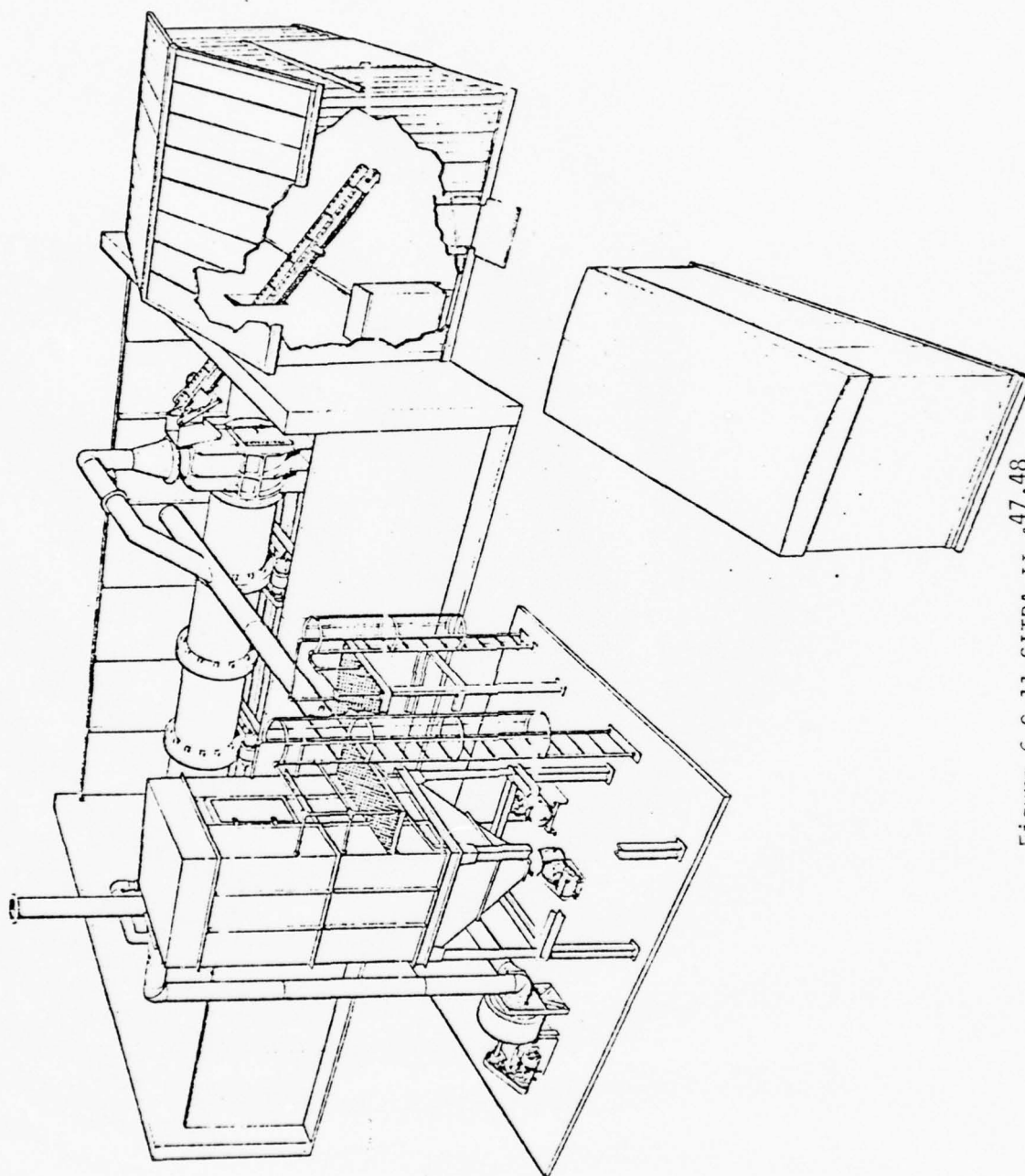


Figure 6.C-11 SITPA II-A^{47,48}

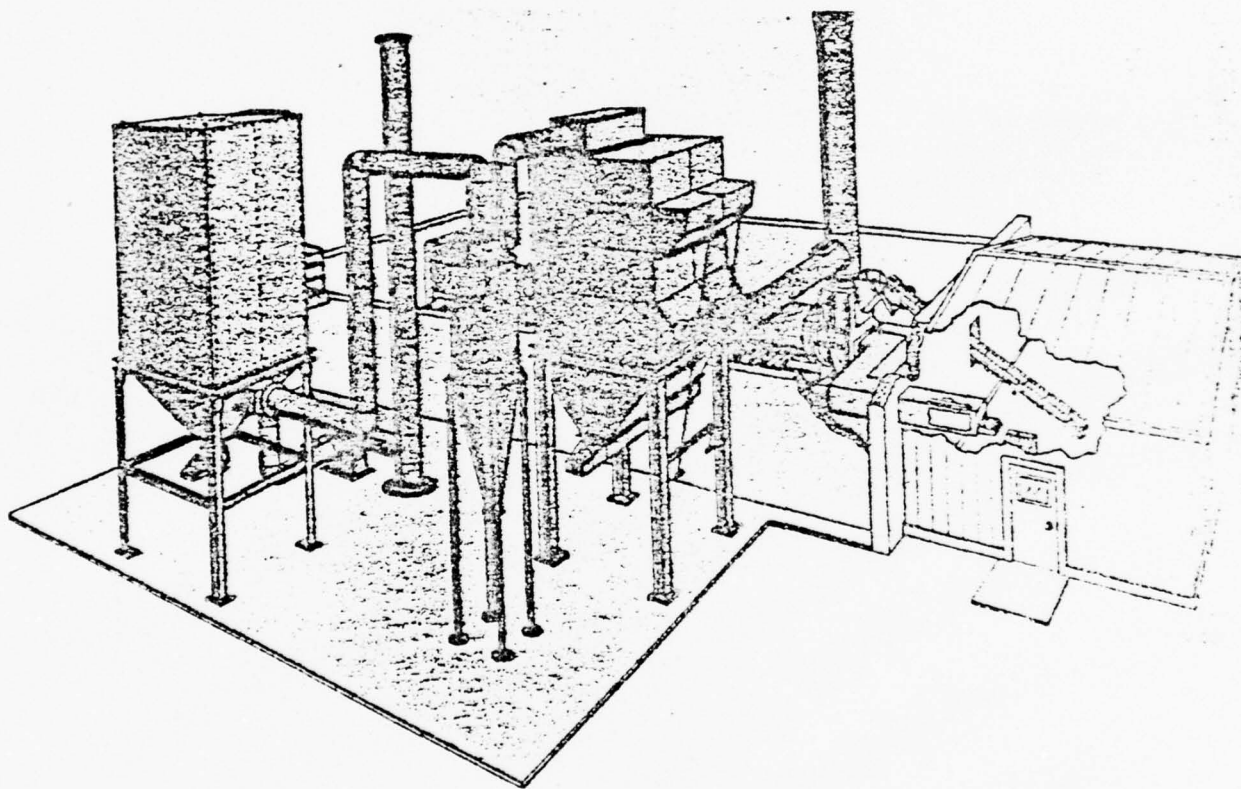


Figure 6.C-12 SITPA II-B 47,48

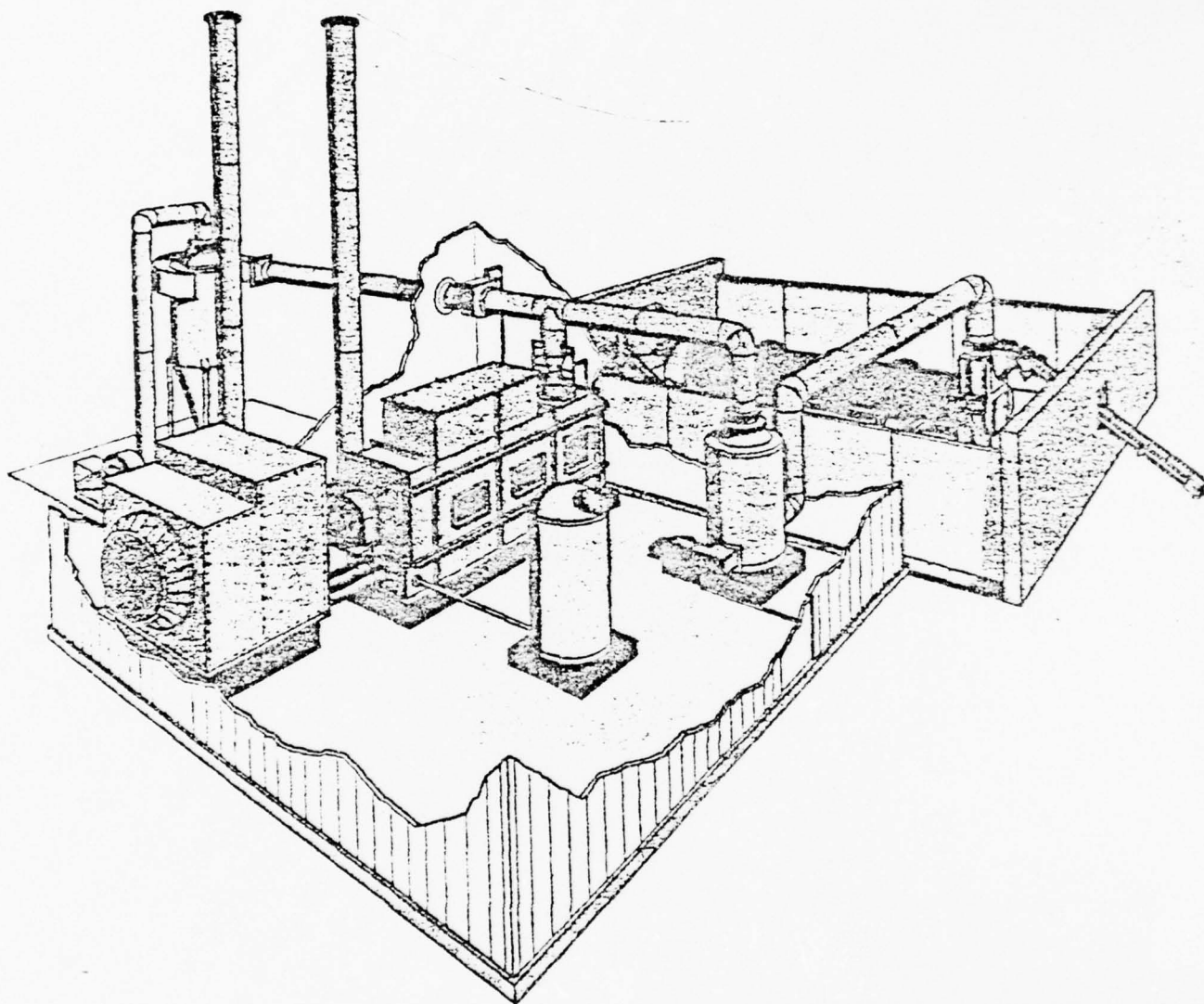


Figure 6.C-13 SITPA II-C^{47,48}

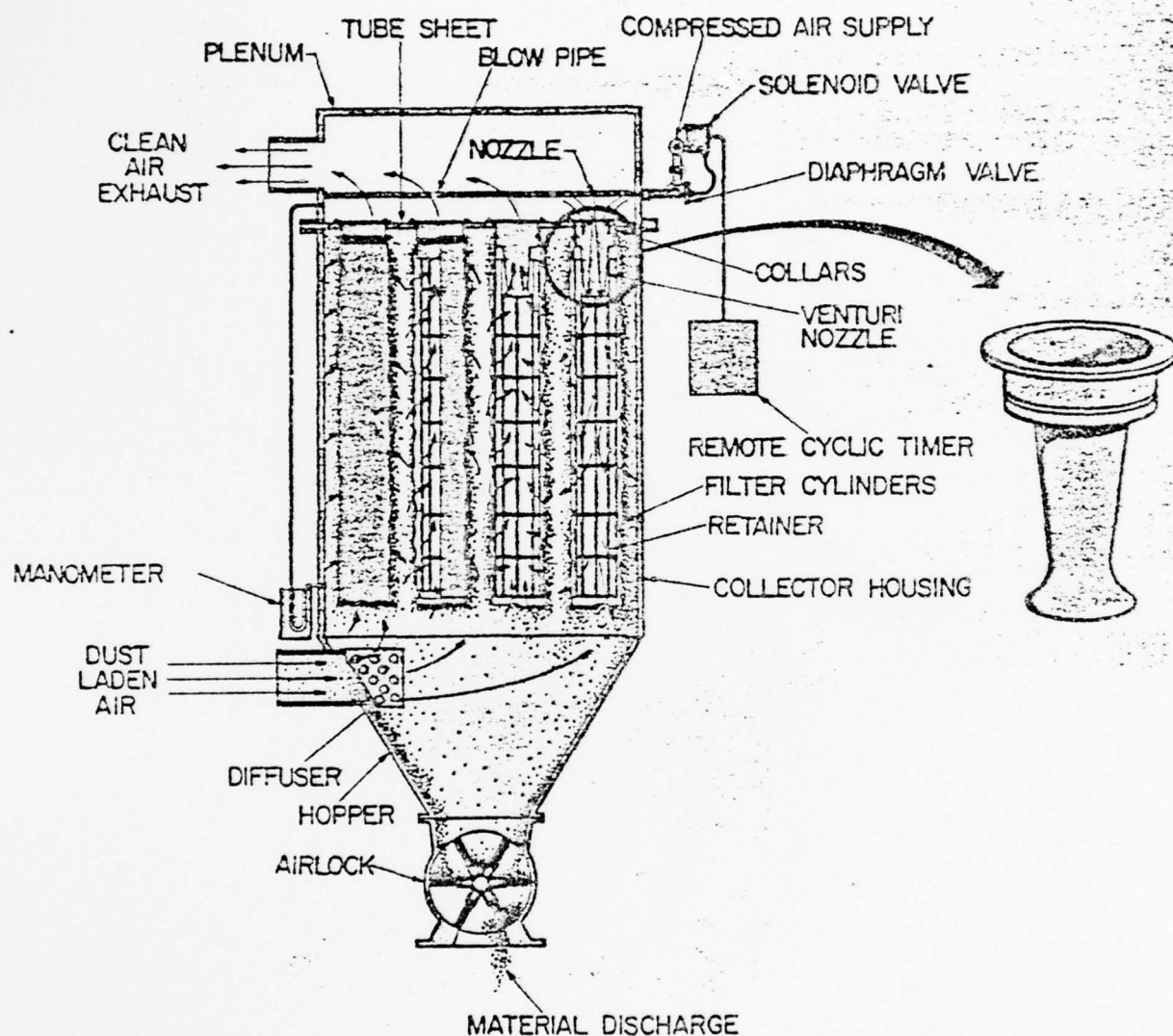


Figure 6.C-14 SITPA II cutaway of baghouse 47,48

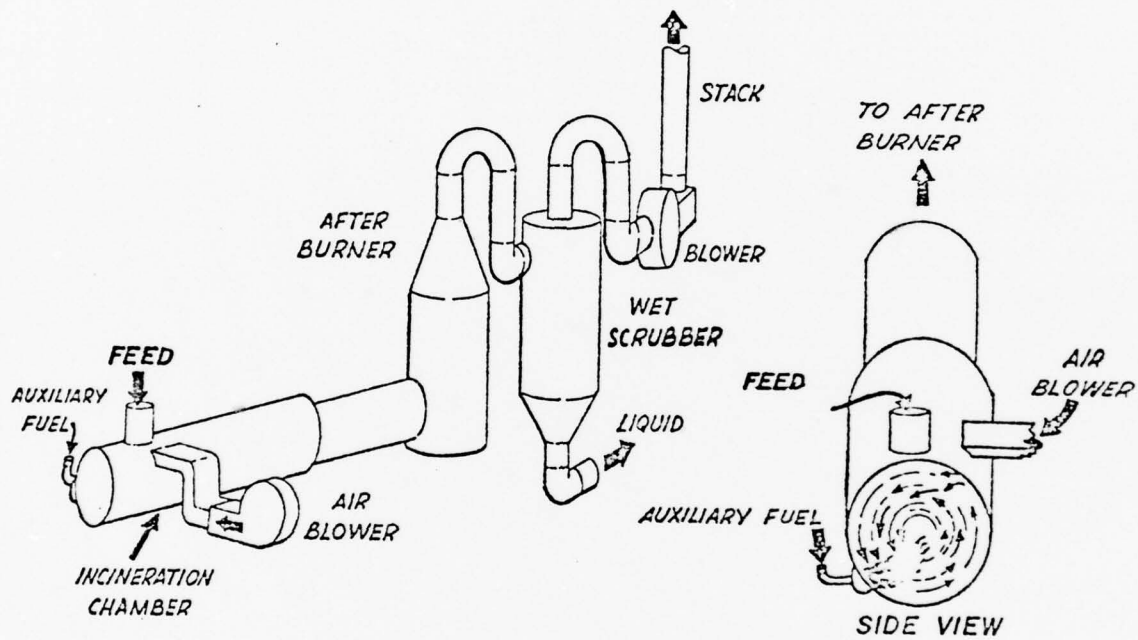


Figure 6.C-15 Vortex Incinerator 39,49

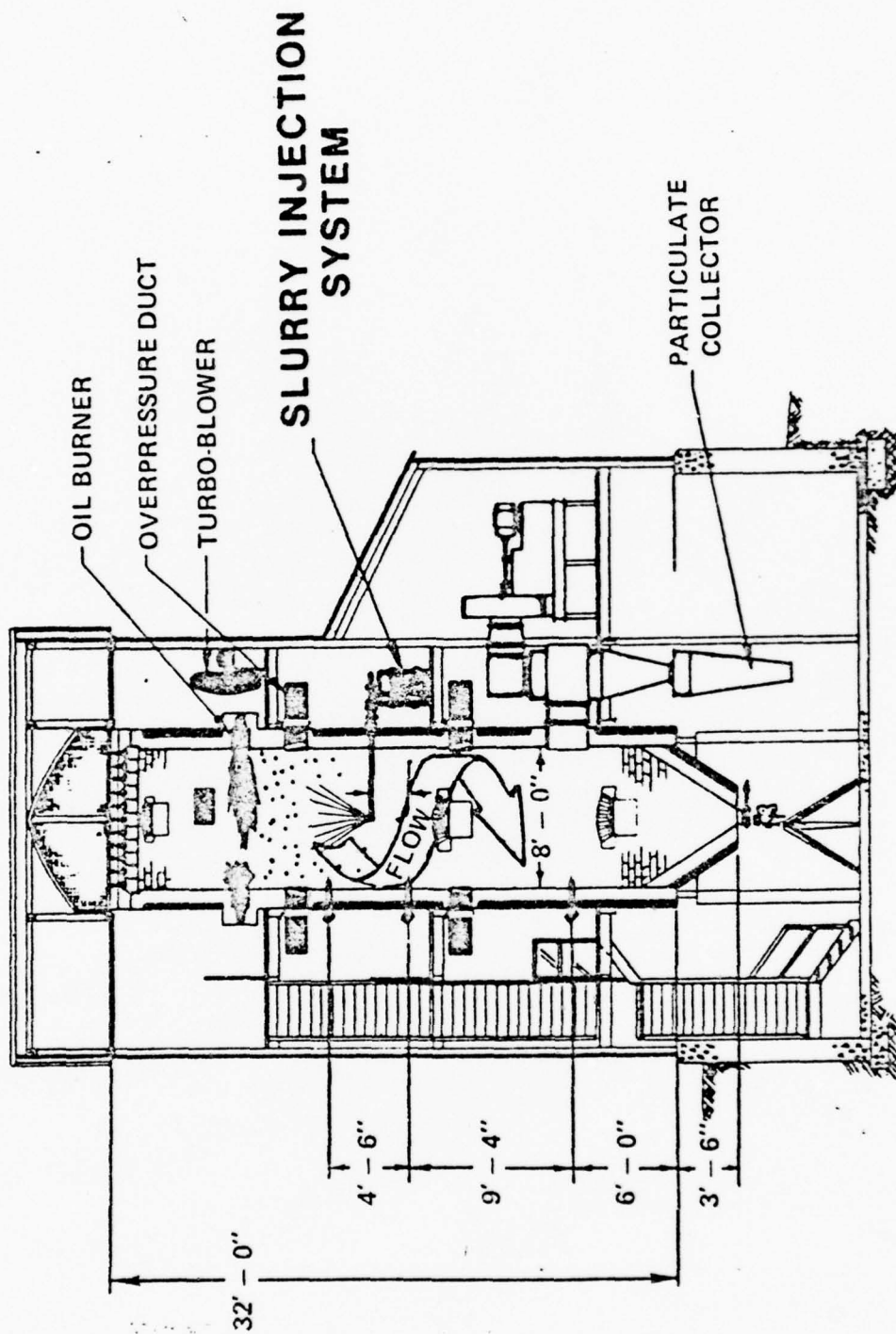


Figure 6.C-16 Vertical Induced Draft Incinerator³⁹

Multiple Chamber Incinerator^{39,50}

A commercial dual chamber induced draft incinerator with a nominal capacity of 600 lbs/hr was procured, installed, and operated at JAAP. A ram feed system was developed to safely inject explosives contaminated waste (dunnage) into the ignition chamber. The combustion chamber, located directly above the ignition chamber, oxidized residual carbon particulates, carbon monoxide (CO) and hydrocarbons (HC). The prototype incinerator successfully burned explosives contaminated wastes with stack emission characteristics well below the standards of the State of Illinois and the U. S. Environmental Protection Agency. Water is not mixed with the waste feed nor used to scrub the effluent gases. Construction costs and operating complexity are negative features of this system. In addition, the explosives contaminated waste is restricted to material that can be compacted to bales measuring 36 x 36 x 18 feet. Reducing the size of explosives contaminated waste is not considered a safe operation.

Incinerators with Best Potential

If one considers the construction and maintenance costs, simplicity of operation, and pollution abatement effectiveness as the criteria in the selection of incinerators for explosives destruction then

SITPA II,
Rotary Kiln, and
SITPA I

would appear to be the choices. Some of the other incinerators may have certain specific advantages, for example, fluidized bed--very low NO_x emissions; however, we feel that economics and simplicity of operation should be one of the more important general criteria in the selection of any incinerator.

Materials Incinerated

Explosives

Because of the limited incineration work that has been done on explosives and explosives contaminated wastes in general, the work at RAAP and Tooele Army Depot and data from Newport, Indiana constitute the basis of this

section of the report. The materials that have been incinerated in the RAAP pilot-scale rotary kiln incinerator are listed in Table 6C-16. The materials incinerated in the rotary furnace incinerator, SITPA I, and SITPA II at Tooele Army Depot are much more varied. They include all the explosives listed in this report in addition to various organometallics, primers, fuzes, and incapacitating chemicals. Tooele Army Depot has compiled one of the most complete computer card files of combustible compositions of munitions available anywhere and is often called upon to deactivate most of them. The incinerators at Tooele are operated as a part of the demilitarization system with a goal to conserve energy by recovering various materials (metals and explosives) and by disposing of toxic materials in an ecologically acceptable manner.

TABLE 6C-16 TYPICAL EXPLOSIVES WASTE MATERIALS INCINERATED AT RAAP³

Explosive/Propellant	Principal Ingredient
Nitrocellulose (NC)	NC
TNT	TNT
Nitroglycerine (NG)	NG + cellulose
Single base propellants	NC, dinitrotoluenes
Double base propellants	NC + NG
Triple base propellants	NC + NG + nitroguanidine
High energy propellants	NG slums
Rocket casting powders	NC, NG, HMX, ammonium perchlorate
Cast and solventless rocket grains	Ammonium nitrate
Rolled sheet propellants	HMX

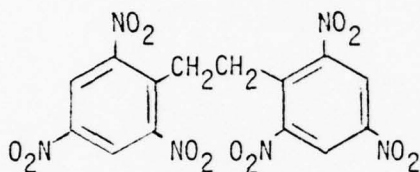
MATERIALS INCINERATED FROM OTHER FACILITIES

Compositions A 1-6	RDX, wax
Composition B	TNT, RDX, wax
Composition C-4	RDX, di(2-ethylhexyl sebacate)
HMX	HMX
RDX	RDX
ABL type (C-3 CMDB)	NC, NG, Al ^o

Red Water

"Red water" is the name commonly applied to the effluent from the sellite (sodium sulfite) purification treatment of crude TNT. The sellite reacts with the unsymmetrical isomers of TNT and other impurities, such as tetra-nitromethane and nitrocresol, and converts them into water soluble sulfonates which are then washed from the main body of TNT. The reactions involved have been summarized in Table 6C-17.

The deep red color of the spent sellite solution is attributed to the presence of hexanitrodibenzyl:



This is a condensation product of two 2,4,6-TNT molecules in the presence of base-stabilized sulfonate salts of the byproducts.

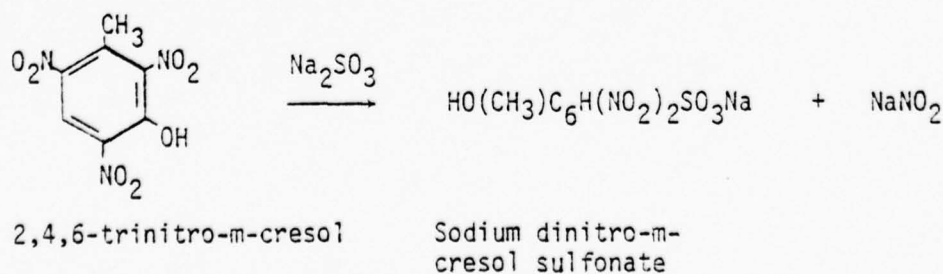
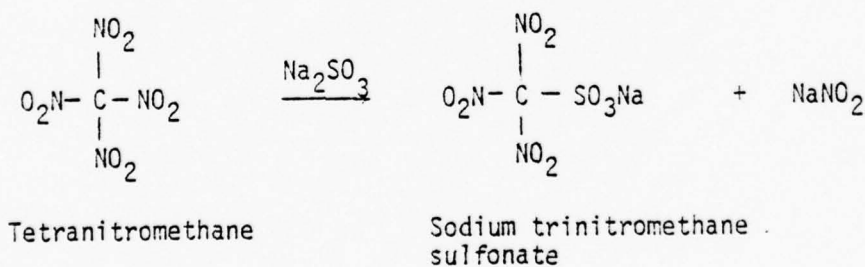
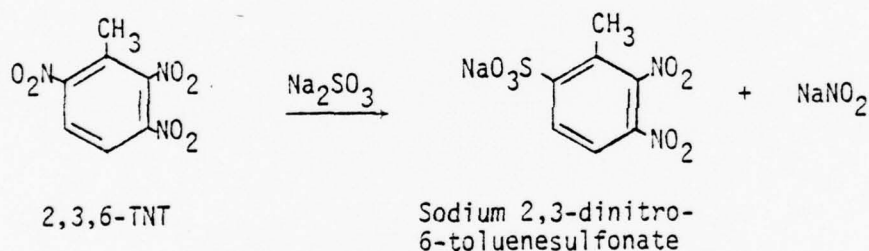
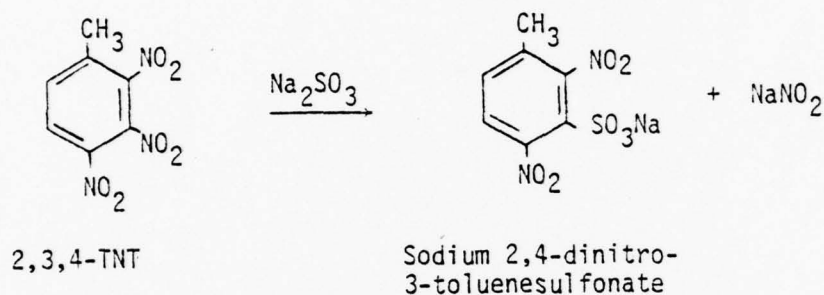
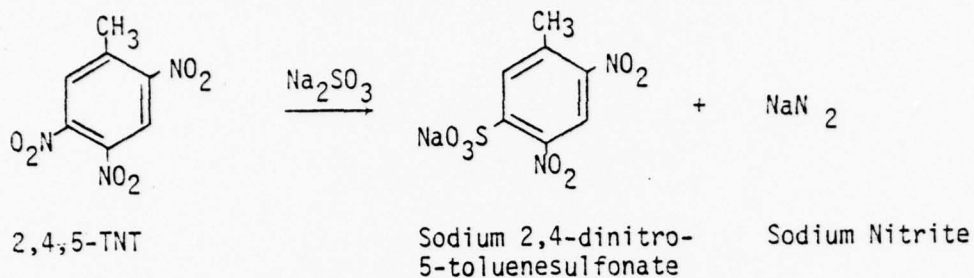
"Red Water" from the purification area of the TNT process has the following approximate composition:

	<u>%</u>
H ₂ O	77.6
NaNO ₃	1.7
NaNO ₂	3.5
Na ₂ SO ₄	0.6
Na ₂ SO ₃	2.3
Organics	14.3

The organic material is mainly a mixture of the water soluble sulfonates of the TNT impurities, plus a small amount of dissolved and entrained TNT.

Concentration and/or incineration of red water can become quite a significant activity at a plant especially when there are no outside customers to sell it to. Thus, RAAP, VAAP, JAAP, and NAAP all concentrate or incinerate red water. RAAP has not operated TNT since 1974. At the next startup, in 1979, all red water will be sold for an undetermined period of time.

TABLE 6C-17 REACTIONS IN SELLITE TREATMENT OF TNT



Quantities of Materials Incinerated

Explosives

Because of the still limited incineration activity for the disposal of explosives, only the data from RAAP's prototype waste explosives incinerator and Tooele Army Depot's deactivation work are available. In the evaluation of the prototype incinerator, approximately 120,000 lbs of propellants and explosives were incinerated at RAAP. Tooele Army Depot had deactivated 150 tons of munitions during 1976 and plans to deactivate 200 tons during 1977. Using the data from one of the AEO⁴⁷ reports, these amounts of munitions may be projected into 48,800 lbs and 54,500 lbs of explosives, respectively. These amounts comprise an extremely wide variety of explosives compositions including organometallics, primers, fuses, and incapacitating chemicals.

Red Water

Of the thousands of different explosive and propellant compositions used, only four basic explosives:

TNT
Nitrocellulose
RDX
Nitroglycerine

comprise the main explosives tonnage and TNT is the most important of the four (Figure 6.C-17)⁵¹. Thus, in the 1969-1971 production period approximately

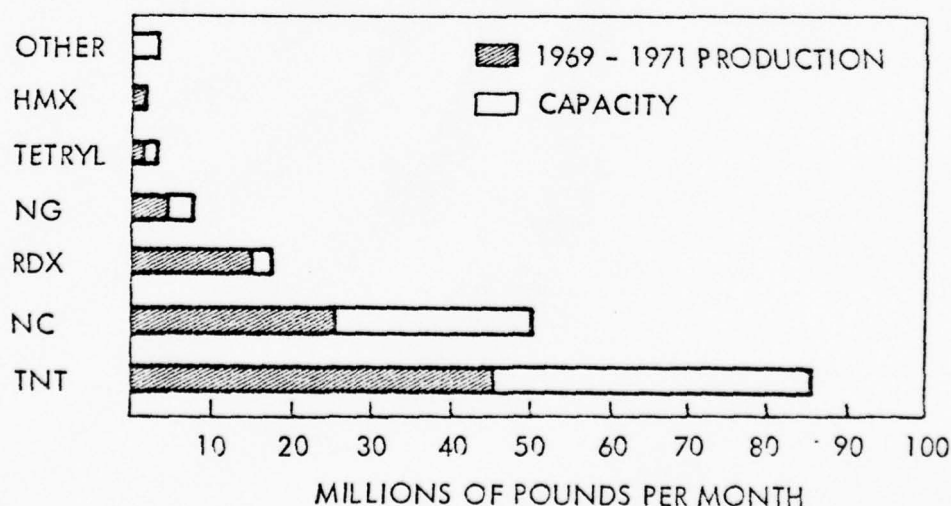


Figure 6.C-17 Production of basic explosive and propellant materials.

45 million lbs of TNT per month were produced. The capacity production at the three facilities is projected to be:

VAAP	500,000 lbs/day
RAAP	150,000 lbs/day
Newport, Indiana	530,000 lbs/day

Using 340 production days per year as a basis, these amounts translate into the following yearly capacities:

VAAP	204 MM lbs/year
RAAP	51 MM lbs/year
Newport, Indiana	180.2 MM lbs/year

Using the Newport, Indiana facilities standard operating manual data for production of 180.2 MM lbs of TNT per year, the following amounts of red water generated can be projected:

	M lbs/day		MM lbs/year	
	<u>100%, 120% of Capacity</u>		<u>100%, 120% of Capacity</u>	
VAAP	415	---	141.2	---
RAAP	104	---	35.3	---
Newport	367	439	124.6	149.5

According to the Newport facilities standard operating manual data red water consists of:

Water	77.6%
Inorganic Salts	8.1%
Organics	14.3%

Thus, at the projected full capacity operation, the following amounts of "organics" in red water are generated:

VAAP	59,000 lbs/day
RAAP	15,000 lbs/day
Newport, Indiana	53,000 lbs/day

These amounts of organics are, therefore, subject to potential concentration or destruction by the plants. From all the literature that we have seen, there appears to be entirely too little attention paid to the details of disposal of these large quantities of organics.

For example, a brief general description of how red water is processed at JAAP is as follows.⁵² There are six four-stage evaporators with a total capacity of 531 gpm and 12 rotary kiln incinerators with a total capacity of 50 gpm. The evaporators concentrate the red water to about 35 percent solids content for incineration in the rotary kilns. The ash from the incinerator is accumulated in an open area within the manufacturing area. The condensate from the evaporation step has a characteristic pale yellow color, contains a small amount of nitrobenzenes and is discharged to the TNT ditch which empties into a creek. The incineration of the concentrated red water generates air pollutants including particulates and nitrogen and sulfur oxides. Based on average discharge data, 3.8 lbs of particulates and 28 lbs of nitrogen oxides (as NO₂) per ton of TNT manufactured are generated.

Combustion Products Generated

National Estimated Incinerator Emissions for 1968

To put the potential emissions from incineration in perspective, they should be compared with those generated from incineration of municipal solid waste in the United States. For this purpose, the data from a study conducted by Arthur D. Little, Inc., was used.⁵⁶ The estimated national incinerator emissions data, Table 6C-18, was arrived at by collecting data from a wide variety of

TABLE 6C-18 ESTIMATED INCINERATOR EMISSIONS FOR 1968
(THOUSANDS OF TONS PER YEAR)

Pollutant	Furnace	Stack
Carbon Monoxide	280	280
Mineral Particulates	90	56
Combustible Particulates	38 } 128	32 } 88
Sulfur Dioxide	32	32
Nitrogen Oxides	26	22
Hydrocarbons	22	22
Hydrogen Chloride	8	6
Volatile Metals (lead)	0.3	0.3
Polynuclear Hydrocarbons	0.01	0.005
TOTAL	496	450

sources and was correlated, as nearly as possible, with refuse composition and incinerator design characteristics and operating parameters. Estimates of the potential pollution load, both uncontrolled and abated by air pollution control devices, were provided by combining the resulting emission factors with the incinerator inventory. The study showed that an incineratory capacity of some 90,000 tons per 24 hr day existed in the United States in 1968. Carbon monoxide and particulates (both mineral and organic) constitute by far the two most abundant pollutants from the incinerator of municipal solid waste.

Combustion Products Sampled

Explosives --

The RAAP prototype incinerator evaluation exhaust gas analysis is summarized in Table 6C-19.³ As it can be seen from this data, the NO_x concentration was maintained around 200 ppm (the set goal) with some exceptions (285 ppm highest and in many cases below 200 ppm). The other pollutant that exceeded its set goal (10 ppm) was H_2S with concentrations as high as 79 ppm. None of the other components (HC , NO_2 , SO_2) measured exceeded the goals set.

Some of the Tooele Army Depot test data on a rotary furnace incinerator (APE 1236 Deactivation Furnace) are presented in Tables 6C-20 - 6C-23. As can be seen, without the pollution abatement equipment, the NO_x concentrations can be very high; with certain munitions, there may be a sulfuric acid mist problem; and the hydrocarbons generated consist mainly of methane plus a variety of other saturated and unsaturated hydrocarbons. However, when the pollution equipment is included, or the SITPA II system is used, the NO_x concentrations as well as those of the other pollutants are lowered significantly. For example, in the destruction of the ABC-M25A2CS riot hand grenades at the feed rate of six grenades per minute, the stack NO_x concentration was only in the 75-150 ppm range and particulates were released at a rate of 0.14 lb/hr.⁵³

TABLE 6C-19 PROTOTYPE ROTARY KILN INCINERATOR EXHAUST GAS ANALYSIS

Type of Material	N ₂ , %	O ₂ , %	CO ₂ , %	HC, ppm	H ₂ S, ppm	NO, ppm	NO ₂ , ppm	SO ₂ , ppm
IMR-EDB	79.22	14.17	5.13	9	0	178	38	0
IMR-EDB	80.51	14.53	5.03	0	0	105	180	0
IMR-EDB	77.17	16.55	2.51	21	74	98	2	5
EDB-BS-NACO	84.68	14.35	5.08	82	65	79	0	0
EDB-BS-NACO, Comp B	---	---	5.10	0	7	130	12	3
IMR-NC-NG	79.02	13.06	5.55	8	14	179	2	4
Neutralized Caustic	---	---	6.00	0	59	11	22	11
Neutralized Caustic	---	---	7.50	35	2	78	4	0
IMR-EDB-NC-NG-TA	---	---	5.06	35	0	138	124	10
EDB-Green Line Scraps	---	---	5.10	41	0	71	148	0
TNT	---	---	3.20	40	39	140	5	0
TNT	80.19	12.64	5.92	0	17	196	33	0
TNT	78.96	12.17	7.14	0	75	189	83	73
ABL 2912	80.36	14.89	4.61	0	12	160	12	18
ABL 2912	78.26	14.17	4.58	0	10	181	77	11
ABL 2912	77.71	15.42	3.85	0	0	165	28	33
HMX	79.98	11.29	7.62	8	7	61	6	11
Comp B	---	---	6.28	30	13	145	14	0
Comp B	---	---	7.60	0	15	120	0	0
Comp A-5	78.29	11.63	7.58	0	33	183	4	51
Comp A-5	78.01	11.15	7.58	0	62	151	1	49
Comp A-5	77.30	12.05	7.18	0	79	81	0	22
Comp A-5	81.44	13.12	7.14	0	5	160	32	2
Comp C4 and Basin Scrap	80.92	11.62	7.39	49	13	162	28	27
Comp C4 and Basin Scrap	81.01	12.41	6.56	58	17	168	22	19

TABLE 6C-20 SUMMARY OF GASEOUS EMISSION DATA - YORK RESEARCH CORPORATION⁴⁷

Munition	Test No.	Stack Flow scfm(1)	Stack Temp °F	H ₂ O Content vol. %	CO ₂ Content vol. %	Ave NO _x ppm	Ave SO ₂ ppm	Ave H ₂ SO ₄ ppm	HCl ppm
Cartridge, 7.62mm Ball M80, Tracer M62	P7	1172	481	4.2	3.8	3326			1.0
	P8	1165	511	4.8	3.8	2312			1.0
Cartridge, Caliber 30 Tracer M1	P2	1156	536	4.4	3.6	7732			
	P3	1094	560	5.4	4.4	8178			
Cartridge, Caliber 50 Tracer M17	P6	1045	619	7.0	5.2	4732			0.4
	P16	1160	532	4.9	3.0	4536			0.1
Cartridge, Caliber 50 API M8	P4	1178	494	6.2	3.7	6799			0.2
	P5	1123	534	7.1	5.5	8681			0.5
Booster, M21A4 Assembled	P14	1267	431	4.8	3.2	117			
	P15	1282	436	4.4	2.4	75.2			
Booster, M21A4 Disassembled	P11	1160	438	3.3	3.0	538			
	P12	1119	475	3.2	3.2	285			
Fuze, MTSQ	P17	1276	432	4.6	4.7	460			1.0
M502 W/M21A4 Booster	P18	1307	392	5.0	3.8	531			1.0
Fuze, Base Detonating M66A1	P19	1259	429	5.6	3.2	163			0.1
	P20	1243	444	5.4	3.8	67.1			1.0
Primer, Percussion M28B2	P9	1150	471	5.1	4.4	49.2	39.5	282.4	0.8
	P10	1122	469	5.1	4.2	40.6			2.0
Primer, Percussion M40A2	P22	1222	453	6.6	4.3	68.6	18.8	53.2	3.0
	P23	1196	436	6.3	4.4	52.9			2.0

(1) 70°F, 29.92 in. Hg

TABLE 6C-21 SUMMARY OF PARTICULATE EMISSION DATA - AEO FOLLOW-ON TESTS⁴⁷

Munition	Test No.	Feed Rate Per Hour	Stack Vel ft/sec	Stack Flow scfm(1)	Stack Temp °F	H ₂ O Content vol. %	CO ₂ Content vol. %	Concentration gr/scfd	Mass Rate lb/hr	Percent Isokinetic
Cartridge, 76mm APC-T M62A1	P10	391	43	1012	513	7.5	4.6	0.612	5.31	128
Shell, 90mm M71 (sawed in two)	P11	85	42	1040	470	5.4	5.4	1.242	11.07	108
Propellant, Class 2	---	300	48.7	926	700	---	---	3.51	27.85	---

(1) 70°F, 29.92 in. Hg

TABLE 6C-22 SUMMARY OF NO_x EMISSIONS DATA - AEO FOLLOW-ON TESTS⁴⁷

Munition	Flow scfm	Average Concentration ppm, Vol	Average Emission Rate lb/hr
Cartridge, 7.62mm Ball M80, Tracer M62	1205	859	7.2
Cartridge, Caliber 30 Tracer M1	1134	5491	44.9
Cartridge, Caliber 50 Tracer M17	1111	7361	58.7
Cartridge, Caliber 50 API M8	1111	6407	51.3
Booster, M21A4 Assembled	1250	653	5.6
Booster, M21A4 Disassembled	1190	1187	10.0
Fuze, MTSQ M502 W/M21A4 Booster	1206	774	6.7
Fuze, Base Detonating M66A1	1206	205	1.8
Primer, Percussion M28B2	1186	113	1.0
Primer, Percussion M40A2	1186	155	1.4

TABLE 6C-23 HYDROCARBON DATA - AEO FOLLOW-ON TESTS⁴⁷

Compound	MUNITION (ppm by volume)						
	Cart., Cal 30 Tracer M1	Cart., Cal 50 Tracer M17	Cart., Cal 50 API M8	Cal 50	Fuze, MTSQ M502	Fuze, B,D M66A1	Primer, Perc M40A2
Methane, CH ₄	2	52	18		2	Trace	1
Ethane, C ₂ H ₆	Trace	Trace	1		---	---	---
Ethene, C ₂ H ₄	3	26	30		Trace	---	1
Propane, C ₃ H ₈	---	---	---		---	---	---
Propene, C ₃ H ₆	1	1	3		Trace	---	Trace
Butane, C ₄ H ₁₀	---	---	---		---	---	---
Butene, C ₄ H ₈	---	Trace	Trace		---	---	Trace
C ₅ +	---	---	---		---	---	---
TOTAL	6	78	52		2	Trace	2

Red Water--

Using the JAAP capacity TNT production rate as the basis, the following amounts of pollutants were projected to be emitted in red water incineration:⁵⁴

NO_x 16,800 lbs/day
Particulates 3,600 lbs/day
SO₂ 1,150 lbs/day.

The RAAP red water destruction complex utilizes four rotary kilns to evaporate the liquid waste. Red water is evaporated to dryness and the nitro-bodies are incinerated leaving behind ash. A summary of the Red Water Destructor No. 2 Unit data are given in Table 6C-24.⁵⁵ These data again emphasize the need for closer attention to red water destruction techniques because of the emission of large quantities of NO_x, particulates, and nitrobodies. Furthermore, in none of the reports that we have seen has the composition of the emitted nitrobodies from the red water destruction process been analyzed.

TABLE 6C-24 EMISSIONS FROM THE RED WATER DESTROYER

	Average	Range
Stack temperature	170°F	155 - 180
Stack gas velocity	3150 ft/min	2020 - 4120
Stack flow	2920 scfm	1840 - 3750
Stack flow percent moisture	45%	43 - 50
Particulate emission rate	0.2 lb/hr	0.1 - 0.4
SO _x emission rate	2.7 lb/hr	2.0 - 4.2
NO _x emission rate	52.6 lb/hr	27.2 - 84.9
NO ₂ emission rate	44.6 lb/hr	35.0 - 61.8
Total nitrobody emission rate	2.3 lb/hr	1.6 - 3.2

Possible Other Combustion Products as Deduced From Relevant Work

U.S. Public Health Service, Division of Air Pollution, has undertaken a program of field sampling to obtain measurements of pollutant emission levels not only from open burning but also from various incineration sources. In addition to obtaining overall emission data, a primary objective of the study was to establish the amounts of polycyclic aromatic hydrocarbons released in incineration. Some of this data are summarized in Table 6C-25. Another study of polycyclic aromatic hydrocarbon formation by incomplete combustion of municipal refuse in a continuous feed incinerator, performed in England, confirmed the general findings of the U.S. Public Health Service that significant amounts of polycyclics can be generated in incineration.⁵⁷ Some of these data are summarized in Table 6C-26. A further study on the evaluation of methods for chemical and biological testing of industrial particulate emissions showed that specific species in addition to polycyclic hydrocarbons were occluded with the particulates.⁵⁸ For example, using high resolution mass spectrometry on the vaporized constituents of the particulate samples from a municipal incinerator, the species summarized in Table 6C-27 were shown to be present.

A rather detailed study of chemical species in the flue gas of a municipal incinerator was performed by Carotti and Kaiser.⁵⁹ They analyzed for organic and inorganic species and examined the C₁ to C₅ hydrocarbon fraction for components in detail. Some of their data are recorded in Tables 6C-28 and 6C-29. Of significance in this study is the fact that very high chloride values (HCl) were found in the flue gases. Furthermore, the concentration of organic acids was comparable to those of NO_x and SO₂. The presence of significant concentrations of fluoride is also of interest. Finally, a considerable variation in the concentration of the most predominant chemical species was experienced probably reflecting variations in the composition of the fuel charge incinerated.

Thus, all of the studies of incineration have shown a rather large variety of gaseous species in addition to polycyclic hydrocarbons as components of the incinerator emissions. It is only a fair projection that such emissions

TABLE 6C-25 POLYCYCLIC HYDROCARBON CONTENT OF PARTICULATE MATTER EMITTED IN INCINERATION

Type of Unit	Sampling Point	MICROGRAMS PER GRAM OF PARTICULATE										
		GROUP 1					GROUP 2					
		Benzo(a)-pyrene	Pyrene	Benzo(e)-pyrene	perylene	Benzo(ghi)-perylene	Anthanthrene	Coronene	Anthracene	Phenanthrene	Fluoranthene	Benzo(a)-anthracene
Municipal incinerators 250 ton/day multiple chamber	Breeching (before settling chamber)	0.016	1.9	0.8				0.06			2.2	0.09
	Breeching (before scrubber)	3.3	28	6.5		19		8.2		9.8	2.5	
	Stack (after scrubber)	0.15	3.6	0.97		1.1		1.1			5.5	0.26
Commercial incinerators 5.3 ton/day single chamber	Stack	58	350	49	3.3	98	7.1	23	51	150	240	5.0
	Stack	180	2600	186	36	540	45	130	53	62	2400	210

TABLE 6C-26 DAILY EMISSIONS OF POLYCYCLIC AROMATIC
HYDROCARBONS IN INCINERATION

Compound	STACK GASES	
	Mg/1000 m ³	Mg day ⁻¹ ^a
Fluoranthene	0.58	274
Pyrene	1.58	745
Benzo(a)anthracene + chrysene	0.72	340
Benzo(b)fluoranthene + Benzo(k)- fluoranthene + Benzo(j)fluoranthene	0.32	151
Benzo(a)pyrene + Benzo(e)pyrene	0.02	9
Perylene	0.18	85
Benzo(ghi)perylene	0.42	198
Indeno(1,2,3-cd)pyrene	0.18	85
Coronene	0.04	19

^a Assuming 12h daily operation; levels measured at flow 655 m³
min⁻¹ corrected to dry, 20°C, 760 mm Hg.

TABLE 6C-27 CONSTITUENTS OF PARTICULATE SAMPLES FROM MUNICIPAL INCINERATOR

Sample Origin	Particle Size (Microns)	Percent of Sample Vaporized	Gases Evolved (@300°C, 10 ⁻⁶ torr)	Hydrocarbon Structures Identified ^b
Municipal Incinerator	1 - 3	4.0	HCN, CO, NO, HCl, CH ₃ CN, CO ₂ , NO ₂ , SO ₂ , CS ₂	Pyrrole, phenol, aromatics through C ₁₀ aliphatic radicals through C ₈
Municipal Incinerator	3 - 10	0.5	HCN, CO, NO, H ₂ S, HCl, CH ₃ CN, CO ₂ , NO ₂ , COS, SO ₂ , CS ₂	Trace hydro- carbons

^a From low ionizing voltage mass spectral data.

^b All isomeric structures are possible.

TABLE 6c-28 CONCENTRATIONS OF CHEMICAL SPECIES IN THE FLUE GASES IN PPM BY VOLUME OF DRY GAS, CORRECTED TO 12% CO₂

Component	TEST NO.									
	1	2	3	4	5	6	7	8	9	10
Nitric Oxide, NO	65.3	72.6	87.6	53.0	69.2	68.8	83.4	56.1	109	115
Sulfur Dioxide, SO ₂	103	102	74.1	58.7	87.9	55.7	132	79.1	143	195
Chloride, Cl ⁻	1250	214	342	402	438	530	455	732	415	417
Cyanide, CN ⁻	<0.09	<0.02	<0.02	<0.04	<0.02	<0.02	<0.03	<0.02	<0.09	<0.10
Fluoride, F ⁻		2.6	6.4	3.8	13.7	10.7	3.0	5.5	14.5	34.2
Phosphate, PO ₄ -3		0.51	0.42	1.00	1.06	0.66	0.89	0.36	4.6	6.3
Organic acids as CH ₃ COOH		35.1	36.7	108	81.8	158	100	116	178	58.2
Aldehydes and ketones as CH ₂ O	12.5	12.6	7.9	2.8	2.4	11.1	5.9	4.6	4.1	5.0
Phosgene, COCl ₂							<0.5	<0.5		<0.5
Chlorine, Cl ₂							<0.2	<0.2		

The CO₂ values ranged from 4-7 percent throughout the tests.

TABLE 6C-29 CONCENTRATIONS OF C₁ THROUGH C₅ HYDROCARBONS IN THE FLUE GASES IN PPM BY VOLUME CORRECTED TO 12% CO₂

Test No.	1	2	3
Methane	<0.4	6.2	13.0
Ethane	<0.4	<0.4	<0.5
Ethylene	1.1	5.6	15.0
Propane	<0.4	<0.4	<0.5
Propylene	<0.4	<0.4	<1.5
i-Butane	<0.4	<0.4	<0.4
n-Butane	<0.4	<0.4	<0.4
i-Pentane	<0.7	<0.6	<0.7
n-Pentane	<0.7	<0.6	<0.7

be also considered in the incineration of explosives and especially explosives contaminated material. Certainly, the air curtain incinerator should be of most concern. Of nearly equal concern should be the rotary kiln and rotary furnace incineration of red water without any pollution abatement equipment.

Thermochemistry Computer Program

In addition to the sampling problems created because of the very wide variety of explosives compositions incinerated, another set of problems is introduced because of the different burning characteristics of the different explosives compositions. Some munitions compositions may burn while others will detonate. They may burn or detonate at distinct intervals; at irregular intervals; or in flurries. As a result, exhaust temperatures will vary greatly and the pollutant emissions may surge and subside as a function of the burning or detonating frequency. Thus, to design an effective sampling program, some prior knowledge or expectation of pollutants from specific explosives compositions is required. The Ammunition Equipment Office, Tooele Army Depot, Tooele, Utah has experimented with a computer program, developed initially for the study of rocket engines, in attempts to predict products of combustion of explosives in the deactivation furnace. The computer program was developed by the Air Force Rocket Propulsion Laboratory at Edwards Air Force Base, California.⁶⁰

The computer program simulates furnace operating conditions; evaluates the chemical compositions of such input data as fuel, air, and munitions consumption rates; considers all species of compounds that may be formed; and predicts the specific products that may exist at furnace stack exit conditions. These data were used to determine which pollutants to sample for.

The computer program is based on a system in equilibrium at a given temperature. The actual furnace process is, of course, a rapid process in which sufficient time for an equilibrium condition may not be provided. For this reason products such as NO_x , which are very dependent on the cooling rate as well as the combustion temperature, are not easily predicted.

A brief description of the kinds of data that can be generated by the computer program on incinerating TNT and a RDX/TNT mixture (Composition B) follows.⁶¹ The combustion species considered by the program on incineration of TNT in the presence of air are listed in Table 6C-30. A typical computer run is illustrated in Table 6C-31. In Tables 6C-32-34 are data that were extracted from the computer runs, converted into grams of species generated per 100 g of TNT incinerated and arranged in decreasing order of the amount generated. Only the species generated in better than 10^{-5} mole per 100 g of TNT incinerated were considered. The effect of two experimental parameters: (1) the amount of air, and (2) the incineration temperature upon the composition of incineration products are examined here. In Tables 6C-32 and 6C-33 are listed the most prevalent species generated at TNT/air ratios of 440 and 1.27 respectively. Thus, the low and high air content incineration results may be summarized as follows.

LOW AIR

1. Many exotic species generated in significant amounts.
2. Among the top six species, two very reactive species: HCN and $\text{HC}\equiv\text{CH}$ are generated.
3. CO is the most abundant component.

HIGH AIR

- No exotic species generated in significant amounts.
- No very reactive species generated among the top six.
- N_2 the most abundant; comparatively little CO generated.

(Text continued on page 483.)

TABLE 6C-30 SPECIES CONSIDERED

C	HNO
CH	HNO ₂
CHN	HNO ₂
CHNO	HNO ₃
CHO	HO
CH ₂	HO ₂
CH ₂ O	H ₂
CH ₃	HCOOH
CH ₄	H ₂ N
CH ₃ OH	H ₂ N ₂
CN	H ₂ O
CNN	H ₂ O ₂
CN ₂	H ₃ N
CO	H ₄ N ₂
CO ₂	N
C ₂	NO
C ₂ H	NO ₂
C ₂ H ₂	NO ₃
C ₂ H ₄	N ₂
C ₂ H ₄ O	N ₂ O
C ₂ N	N ₂ O ₃
C ₂ N ₂	N ₂ O ₄
C ₂ O	N ₂ O ₅
C ₃	O
C ₃ O ₂	O ₂
C ₄	O ₃
C ₄ N ₂	C (Graphite)
C ₅	H ₄ N ₂ (L)
H	N ₂ O ₄ (C)
HN	N ₂ O ₄ (L)

TABLE 6C-31 TYPICAL COMPUTER RUN

COMPUTER RUN DATE JULY 25, 1973

Propellant	HF	Density	Weight	Moles	Volume
TNT	13.0000	1.6000	10.0000	0.0440	6.2500
Air	0.0000	0.0200	50.0000	0.0347	2500.0000

Gram Atoms	C	H	O	N
/100 grams	0.5136	0.3669	1.6533	4.7836

Enthalpy = 0.95392

Density = 0.024

	Chamber
Pressure (PSIA)	13.000
Epsilon	0.000
ISP	0.000
ISP (Vacuum)	0.000
Temperature (K)	2242.350
Molecular Weight	30.088
Moles gas/100 g	3.324
CE	0.000
PEAE/M (Seconds)	0.000
Gamma	1.254
Heat Cap/Cal	32.572
Entropy (Cal)	219.192
Enthalpy (Kcal)	0.954
Density (g/cc)	1.44649E-04
Iterations	5

Moles/100 Grams

C	1.78497E-17	C ₂ H	4.26154E-24	HC ₂	3.51577E-06
CH	8.16988E-19	C ₂ H ₂	7.53907E-24	H ₂	1.09775E-03
CHN	2.41123E-12	C ₂ H ₄	4.09242E-30	HC ₂ OOH	3.40479E-10
CHNO	1.13464E-10	C ₂ H ₄ O	1.82169E-32	H ₂ N	9.44488E-10
CHO	7.91724E-09	C ₂ N	3.73021E-24	H ₂ N ₂	8.47502E-15
CH ₂	1.60100E-19	C ₂ N ₂	5.38652E-23	H ₂ O	1.76684E-01
CH ₂ O	2.98939E-12	C ₂ O	7.69076E-19	H ₂ O ₂	1.62872E-07
CH ₃	9.48545E-19	C ₃	6.66476E-35	H ₃ N	1.62872E-07
CH ₄	9.43391E-20	C ₃ O	8.55680E-23	H ₄ N ₂	2.14199E-10
CH ₃ OH	5.90953E-20	H	4.56107E-04	N	6.08610E-08
CN	5.09288E-14	HN	7.22578E-09	NO	2.56389E-02
CNN	6.46187E-21	HNO	1.85799E-07	NO ₂	1.48150E-05
CN ₂	2.37280E-17	HNO ₂	1.15320E-07	NO ₃	1.56637E-11
CO	1.65518E-02	HNO ₂	1.00373E-07	N ₂	2.37895E+00
CO ₂	4.97095E-01	HNO ₃	1.87624E-11	N ₂ O	1.15196E-06
C ₂	2.45395E-27	HO	1.87624E-02	N ₂ O ₃	7.41238E-14

TABLE 6C-32 INCINERATOR PRODUCTS OF TNT

TNT	0.0440 mole
Air	0.0001 mole
TNT/Air	440
Temperature	1993°C
CO	73.64 g /100 g TNT
N ₂	18.62 g
C, graphite	4.57 g
H ₂	2.12 g
HCN	0.845 g
HC≡CH	0.115 g
H	0.019 g
C ₂ H	0.003 g
CHO	0.001 g
CN	0.0008 g
CH ₄	0.0007 g
CO ₂	0.0005 g
H ₂ O	0.0005 g
CH ₃	0.0003 g

TABLE 6C-33 INCINERATOR PRODUCTS OF TNT

TNT	0.0440 mole
Air	0.0347 mole
TNT/Air	1.27
Temperature	1969°C
N ₂	66.61 g /100 g TNT
CO ₂	21.87 g
O ₂	6.82 g
H ₂ O	3.18 g
NO	0.769 g
CO	0.463 g
HO	0.185 g
O	0.050 g
H ₂	0.002 g
NO ₂	0.0007 g
H	0.0005 g

TABLE 6C-34 INCINERATION PRODUCTS OF TNT

TNT	0.0440 mole
Air	0.0277 mole
TNT/Air	1.59
Temperature	2164°C
<hr/>	
N ₂	64.62 g /100 g TNT
CO ₂	23.87 g
O ₂	4.35 g
H ₂ O	3.67 g
CO	2.07 g
NO	0.891 g
HO	0.365 g
O	0.120 g
H ₂	0.009 g
H	0.003 g
NO ₂	0.0005 g

LOW AIR

HIGH AIR

- | | |
|--|--|
| 4. "Graphite" in significant amount. | No graphite generated. |
| 5. Molecular and atomic hydrogen generated in significant amounts. | Molecular and atomic hydrogen generated in very low amounts. |

Listed in Tables 6C-33 and 6C-34 are the most prevalent incinerator species at 1969°C and 2164°C respectively. Thus, the low and high temperature incineration results may be summarized as follows:

1. Nitrogen is the most prevalent component at both temperatures.
2. The same eleven most abundant species are generated at both of these temperatures.
3. At the higher temperature, almost 5 times more CO generated; 6 times more atomic hydrogen generated; 4 times more molecular hydrogen generated; about 2.5 times more atomic oxygen generated; and about 2 times more hydroxyl radical (HO·) generated.

In summary of these results, it is easily seen how important the air concentration (O₂ concentration) is even in incineration in decreasing multiplicity of possible combustion products. This in turn indicates the important

role fuel-air mixing (turbulence) plays even in incineration if efficient combustion is to be achieved. The available data on the temperature effect is not sufficiently broad to make any significant generalizations. Furthermore the indicated temperatures are probably unrealistically high as incinerator operating temperatures go.

We were not able to obtain computer modelling data on pure RDX; however, data on Composition B (60:40 RDX:TNT) were obtained. In Table 6C-35 are listed all the species considered by the program. In Table 6C-36, we have extracted and calculated the amounts of the most prevalent species, generated in the incineration of Composition B in the absence of air, in larger than 10^{-6} mole amounts.

TABLE 6C-35 SPECIES CONSIDERED

C	CN	C ₂ N	HNO	H ₂ O	N ₂ O ₃
CH	CNN	C ₂ N ₂	HNO ₂	H ₂ O ₂	N ₂ O ₄
CHN	CN ₂	C ₂ O	HNO ₂	H ₃ N	N ₂ O ₅
CHNO	CO	C ₃	HNO ₃	H ₄ N ₂	O
CHO	CO ₂	C ₃ O ₂	HO	H	O ₂
CH ₂	C ₂	C ₄	HO ₂	NO	O ₃
CH ₂ O	C ₂ H	C ₄ N ₂	H ₂	NO ₂	C (graphite)
CH ₃	C ₂ H ₂	C ₅	HCOOH	NO ₃	H ₄ N ₂ (L)
CH ₄	C ₂ H ₄	H	H ₂ N	N ₂	N ₂ O ₄ (G)
CH ₃ OH	C ₂ H ₄ O	HN	H ₂ N ₂	N ₂ O	N ₂ O ₄ (L)

TABLE 6C-36 INCINERATION PRODUCTS OF 60/40 RDX/TNT

	RDX	0.2701 mole
	TNT	0.1761 mole
	Temperature	2305°C
CO	52.32 g	/100 g Composition B
N ₂	30.075 g	O 0.009 g
H ₂ O	8.081 g	O ₂ 0.004 g
CO ₂	7.674 g	CHO 0.001 g
H ₂	1.525 g	N 0.0002 g
HO	0.158 g	HN 0.00002 g
H	0.070 g	H ₂ N 0.00002 g
NO	0.024 g	H ₃ N 0.00002 g

As shown in these tables, numerous very reactive species are generated similarly to TNT in combustion using low air concentration. Likewise, CO is the most prevalent species generated. Differently from TNT/low air, large concentrations of CO₂, H₂O, HO·, and NO are generated. Likewise, numerous hydrogen-nitrogen reactive species are also generated.

Perhaps the strongest signal that this examination of very limited computer modelling data gives is the potential for a very "rich" gas phase chemistry between the various indicated reactive species generated. On the basis of this preliminary examination of computer modelling data, it is strongly suggested that the approach be explored in more detail in future explosives incineration work.

In this connection, RTI, through the cooperation of Messrs. Edward E. Stein, Deputy Chief, Liquid Rocket Division and Curtis Selph of the Air Force Rocket Propulsion Laboratory (AFRPL), Edwards Air Force Base, California has obtained the three main files: (1) input procedures to the program, (2) the thermochemistry program, and (3) the thermodynamic library containing data on the products of combustion, for computer modelling work.

The AFRPL Program is based on the method of "minimization of free energy" first described by White, Johnson, and Dantzig in the Journal of Chemical Physics, 28(5), (1958). This model has been extended to include condensed phases and to allow simultaneous convergence on temperature with constant enthalpy or entropy.

The program models high temperature problems assuming that a condition of chemical equilibrium exists. In general, the higher the temperature, the more reliable the model becomes; but the program is not limited to high temperature calculation. It generates a solution that preserves mass balance for each of the chemical elements, while satisfying the equilibrium expression and an additional constraint related to temperature. Constant enthalpy constraint is the one automatically assumed by the program in the absence of further specification. An assigned temperature option is also available. The AFRPL experience plus the JANAF Thermochemical Data Tables now cover over 1300 products of combustion from 42 chemical elements. Thus,

most any of the explosives compositions to be considered would be expected to be covered by the data available.

In addition, below we have listed pertinent references to computer programs for calculating compositions of high temperature combustion products:

1. Kistler, D. E., Air Force Rocket Propulsion Laboratory Scientific Computer Programs, Air Force Rocket Propulsion Laboratory, Air Forces System Command, US Air Force, Edwards, California, No. AFRPL-TR-69-84. May 1969.
2. Bureau of Mines Circular/1973, IC 8606, PB 225077, Computer Program for Calculating Equilibrium Composition of High Temperature Combustion Products, US Dept. of Interior.
3. MacDonald-Douglas Astronautics Company, BRL-Contract Report No. 107, Estimation of Gas-Phase Thermokinetic Parameters, April 1973. (Approved for public release, distribution unlimited, USA Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland, NTIS.) Prepared under Contract DAAD05-72-C-0098, 3 volumes.
4. McMains, Forest L., Thermochemical Properties of Propellant Formulations by Means of a Computer Program, Tech Memo 1595, Picatinny Arsenal, Dover, NJ, April 1965.

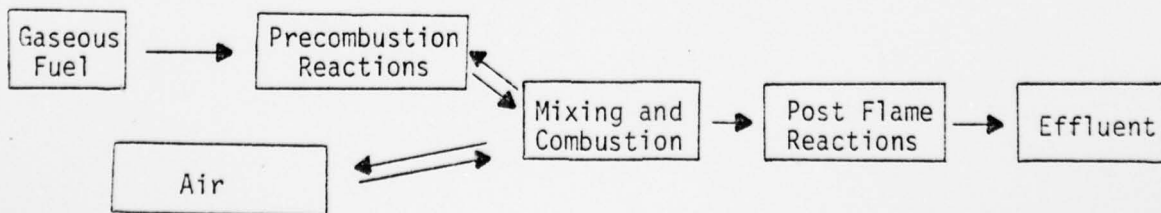
6.C.1.4 Characterization of Combustion

Types of Combustion

The various types of combustion as discussed by Edwards⁶³ will be summarized first. These are diffusion and premixed flames as well as the combustion (detonation) of explosives and propellants. This classification is according to the initial states of the fuel and oxidant. Following this, the evaluation of incineration and the major performance features of incinerators will be summarized from the discussion of Elliott and McCormack.⁶²

Diffusion Flame-Open Burning

The sequential arrangement of precombustion, combustion, and postflame processes in a diffusion flame may be represented as follows:

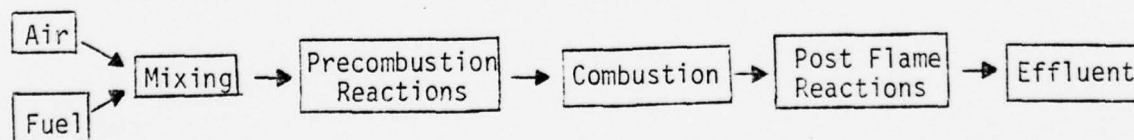


In diffusion flames (open burning) the precombustion reactions occur before mixing of the fuel and air. Thus, in the precombustion zone of a diffusion flame, there are no oxidizing species of the type: O , HO , O_2 , RO , and ROO . The environment for precombustion reactions in a diffusion flame is highly reducing in character. The reaction products are pyrolytic and include unsaturated species such as olefins and acetylenes and particulate nuclei resulting from polymerization or addition reactions between the unsaturated species. The net result of the appearance of particulate species in the precombustion zone is to enhance the thermal coupling between the precombustion and combustion zones and increase the temperature of the gaseous species in the precombustion zone and promote pyrolytic reactions. It is this coupling of zones that drives the pyrolytic precombustion reactions that are generally endothermic.

Another fundamental characteristic of diffusion flames is the mechanism of their ignition. Ignition in a diffusion flame is controlled by the physical processes that influence mixing such as turbulence and the geometry of the system. Furthermore, mixing also has an influence on the composition of the reaction products. If final mixing is poor, the pyrolytic reactions may produce relatively large quantities of particulate material and other pyrolytic reaction species. Thus, it is easy to understand the importance of the mixing step and the propensity of diffusion flames in general to form copious amounts of carbonaceous particulate matter.

Premixed Flame

The arrangement of precombustion, combustion, and postflame processes in a premixed flame may be represented as follows:



One of the fundamental differences of premixed flames is that precombustion reactions occur after intimate mixing of fuel and air. Thus, the precombustion zone in premixed flames does contain reactive oxidizing species such as O , OH , RO , ROO , and O_2 . As the fuel/air mixture enters the precombustion reaction zone, reactions of the following type occur:

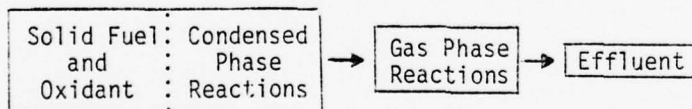


These reactions are promoted by the transfer of heat and active species from the combustion zone.

Ignition in a premixed flame is sustained whenever the quantity of thermal energy liberated by the oxidative precombustion reactions is sufficient to overcome thermal losses from the reacting mixture and raise it to its ignition point. This mechanism is inoperative in the diffusion flame because the fuel is initially separated from the oxidant. Thus, in the premixed flame, ignition is controlled by chemical processes that influence the rate and extent of heat release and the degree of chain branching.

Diffusion and Premixed Flames-Incineration of Propellants and Explosives

The incineration of explosives and propellants involves both types of flames--diffusion and premixed. Typically, the incinerator is oil or natural gas fired generating a diffusion flame and once the explosive is ignited a premixed flame is also generated by the burning explosive. The oxidant in the propellant or explosive is presumably molecularly dispersed and need not always be oxygen. The combustion of propellant may be represented as follows:



The rate of combustion is dependent upon a number of factors: (1) chemical composition, (2) surface area, and (3) the physical state of the propellant. The explosive or propellant may also detonate in addition to burning. In detonation, the gas/solid interface propagates through the solid at the speed of sound in the solid.

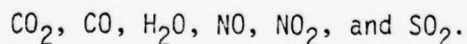
As a result, very high temperatures are generated as the shock wave converts the solid to gaseous reaction products. Because of the very violent nature of propellant and explosive combustion in general, large quantities of particulate matter may be also present in the effluent.

Another factor that influences the combustion products of explosives and propellants is the high temperatures often achieved during combustion. This is followed by rapid expansion and therefore thermal quenching of the reaction products. The high temperatures result because of the intimate mixing of both fuel and oxidant. Without the thermal inertia of the diluent, high temperatures and a greater degree of dissociation into elementary and simple diatomic and triatomic species will be achieved. The rapid expansion that usually follows will tend to preclude recombination reactions forming more complex products. Thus, the reaction products will tend to reflect the species present at peak flame temperatures and pressures.

In summary, a diffusion flame is a more complex process than a premixed one. Physical processes such as evaporation and mixing in addition to complex pyrolysis reactions in the precombustion zone all complicate diffusion flame processes. This is in contrast to a premixed flame where chemical factors are rate determining. Incineration of explosives and propellants is an infinitely more complex process because of the combination of both diffusion and premixed flame processes compounded with detonation processes. Thus, the prediction of a likely product composition is extremely difficult and computer modelling studies of the type undertaken by Tooele Army Depot and by the Research Triangle Institute are needed.

Oxide Formation

The following oxides are the principal components emitted by combustion processes:



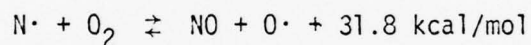
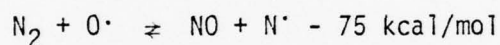
These oxides, with the exceptions of CO_2 and H_2O , have been labeled as serious air pollutants. Actually, even CO_2 on a global basis due to its

contribution to the "greenhouse effect"⁶⁶ and H₂O on a local basis, due to its contribution to visibility-reducing fog have been also labeled as pollutants. Under actual combustion conditions, a host of additional species are emitted all of which are considered air pollutants. However, under "ideal" combustion conditions (equilibrium oxidation) the above oxides are the only species formed from materials containing only C, H, O, N, and S.

NO_x

Nitric oxide, NO, is formed both from nitrogen in the air and from combined nitrogen in the fuel. The formation of this compound is a complex process that involves several elementary chemical reactions. It involves both equilibrium and nonequilibrium processes that take place in the pre-combustion, combustion, and postflame regions.

The following reactions



are referred to as the Zeldovich Mechanism for nitrogen fixation. The chain aspect of this mechanism for the conversion of molecular nitrogen and oxygen to nitric oxide is illustrated in Figure 6.C-18.

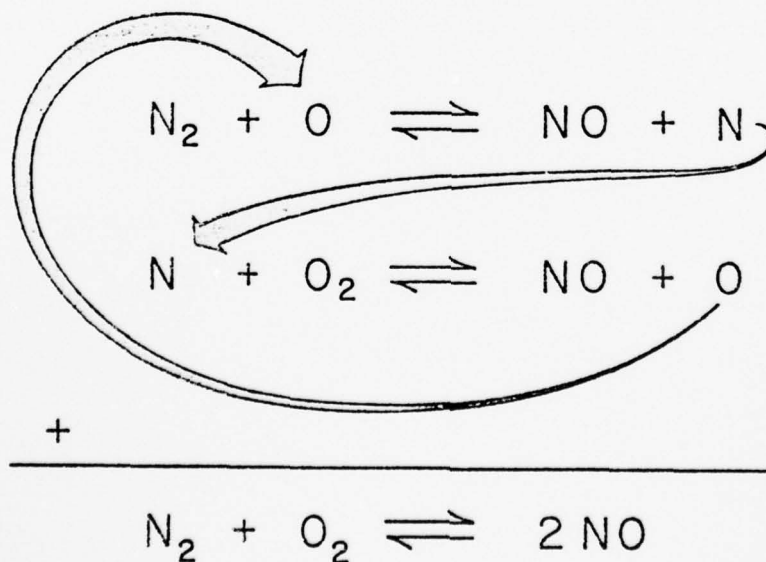
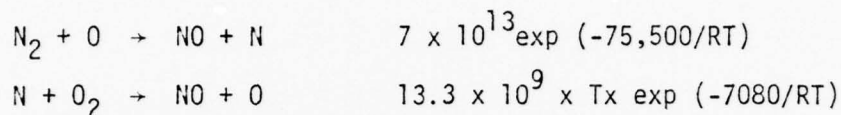


Figure 6.C-18 Chain mechanism for the fixation of nitric oxide.

The higher the temperature, the more NO is formed. The first reaction in the set is by far the slower of the two. The kinetic data for the two reactions are:⁶⁸



rate constant units: $\text{cm}^3/\text{mole-sec.}$

From the above it can be seen that the activation energy for the first reaction is at least an order of magnitude higher (75,500 calories/mole) than the activation energy for the second reaction and is one of the highest values for such reactions in general. Thus, this reaction will take place at an appreciable rate only at high temperatures (above 1600°C or 1900°K). In Figure 6.C-19 the rate constant for the reaction $\text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N}$, using Newhall's rate data,⁶⁸ is plotted against temperature. As it can be seen, the rate constant increases rapidly above 1900°K illustrating the strong temperature dependency of NO kinetics. Thus, NO formation can be restricted by lowering the peak temperature in the combustion process.

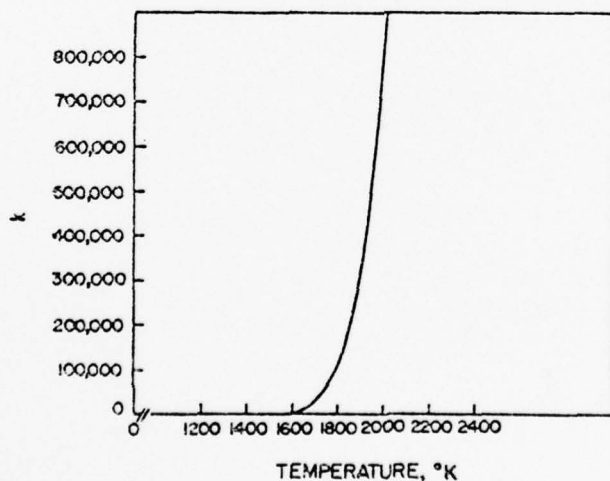


Figure 6.C-19 Dependency of NO kinetics upon temperature.

One procedure to keep NO_x low is to partially combust in a fuel rich system at 980-1100°C followed by some excess air addition and a second stage of combustion.⁶⁹ Another option is to combust rapidly, so that if air nitrogen is the N source, equilibrium is not reached. Such results are discussed by Wassen *et al*⁷⁰ for fuel oil combustion where flame temperatures were determined and NO levels were less than calculated.

In summary of NO formation, the various reaction paths in methane/air combustion are depicted in Figure 6.C-20. The numbers in the complete mechanism were based on 100 moles/sec production rate of NO. It is noted that only 48 moles constituted the actual output.

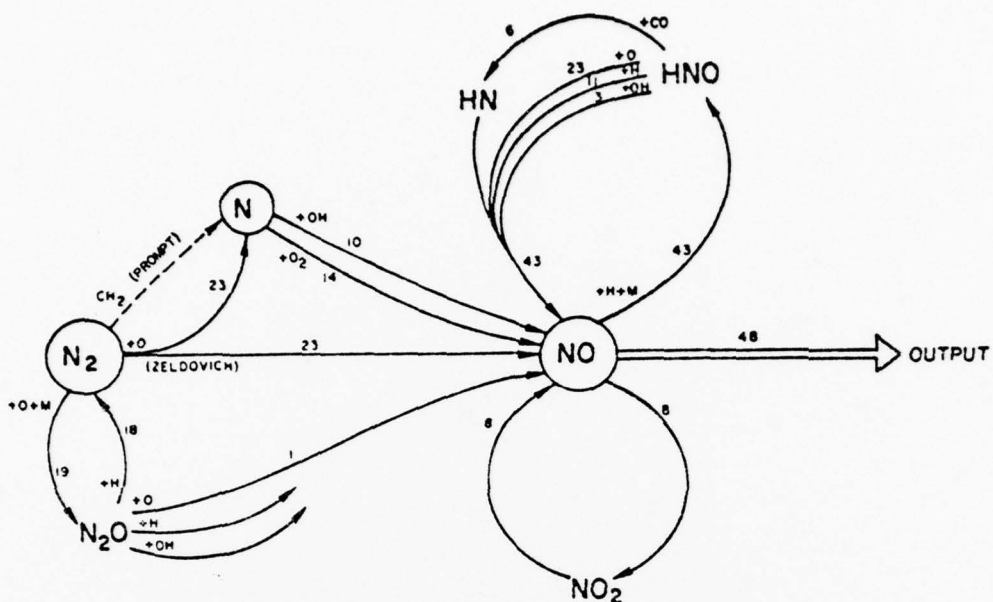
CO and CO₂

Carbon monoxide is formed almost instantaneously in combustion. However, the oxidation of carbon monoxide is kinetically slow and quite sensitive to the temperature and oxygen content of the mixture. Specifically, the oxidation rate is decelerated as the temperature is decreased and the mixture becomes oxygen starved (e.g., fuel-rich flames).

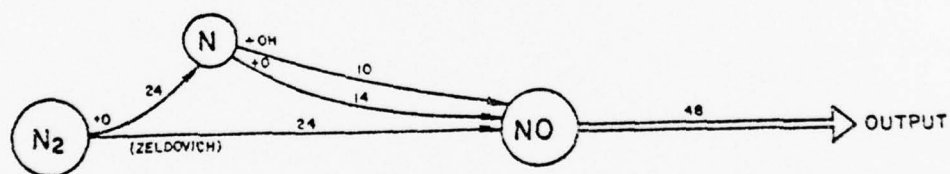
Above 700°C, carbon monoxide is oxidized reasonably quickly in the presence of oxygen. Such conditions are commonly used in continuous combustion systems such as power plants and package boilers. In automobiles, however, the fuel/air mixtures are fuel rich and little time is available at elevated temperatures before the combustion products are exhausted and as a result automobiles are the largest contributor to CO emissions. A summary of CO and CO₂ formation in the methane/air combustion is depicted in Figure 6.C-21. It is noted that the rate numbers are based on 100 moles/sec production rate of CO and CO₂.

SO_x

Sulfur dioxide is formed very fast in combustion if sulfur is present in the fuel. Because it is formed so fast, the kinetic behavior of SO₂ has not been extensively investigated.⁷² Sulfur dioxide/sulfur trioxide ratios are very temperature dependent. The equilibrium values given by Corey⁷³ for the 1600-2400°F range show a shift in SO₃ concentration from 6 to 10 percent of the total sulfur oxides at 1600°F to 0.5-0.8 percent at



Complete Mechanism (stoichiometric mixture). (Based on 134-reaction set for CH_4/air .)



Simplified Mechanism. (22-reaction set for CH_4/air .)

Figure 6.C-20 Chemical kinetic paths for NO formation in CH_4/air combustion.⁷¹

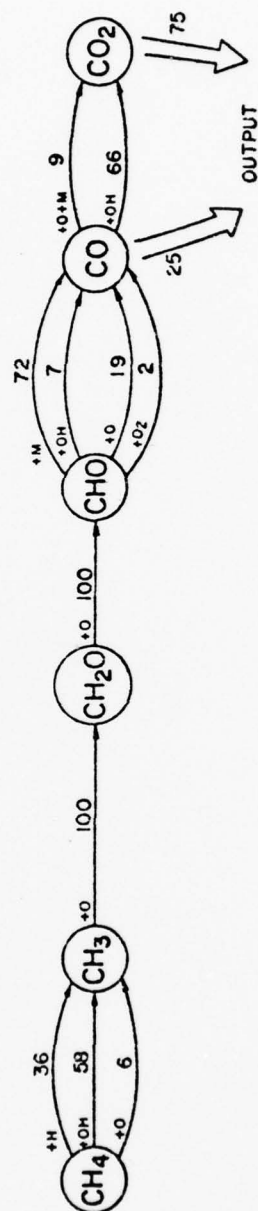
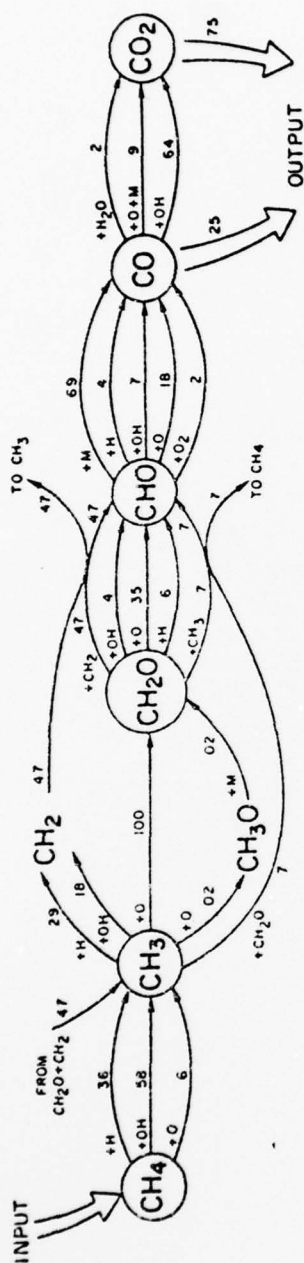


Figure 6.C-21 Chemical kinetic paths for CO and CO₂ formation in CH₄/air combustion.

2400°F for different oxygen levels. Higher concentrations of SO_3 can give sulfuric acid or lead to sulfate formation. Sulfites have been observed in exhaust gases from automobiles operating with oxidizing catalysts. A discussion of elementary reactions of sulfur in flames can be found in References 72 and 74.

Particulate Matter Formation

Basically, particulate matter may originate from inorganic, organo-metallic or the fuel molecules themselves. If inorganic (metallic) matter is present in the fuel, it cannot be destroyed by complete ignition of the fuel. The inorganic (metallic) species are oxidized in the flame and will appear normally as oxides or salts in the postflame gases. The other source of particulate matter is the fuel molecules themselves. Little is known about the exact mechanism of particulate growth from a species of a very low molecular weight (few carbon atoms) to one with tens of thousands of carbon atoms. It is possible that the inorganic oxides and salts mentioned above may act as nuclei for particle growth. Alternatively, at any point of fuel rich conditions in the flame excess pyrolysis will occur with possible formation of condensation products faster than the oxidation can take care of it. At least one study has demonstrated the applicability of this concept, along with the quenching concept, to particulate matter formation.⁷⁰ The formation of carbonaceous condensation products is also discussed by Corey⁷³ and Monroe.⁷⁵

In addition to chemical processes, particles may grow by processes that are essentially physical in nature. Agglomeration of small carbonaceous particles to produce larger aggregates stuck together in a rather open network of a few hundred Ångströms have been observed.⁶³ The particles consist of 10^3 - 10^4 crystallites, each composed of 5-20 sheets of carbon atoms with a length and breadth of 20-30 Å. Chain-like agglomerates from 100-2500 Å may ultimately form. The nature (size, molecular weight, structure) of particles ultimately formed depends upon conditions such as the residence time of the particles in the postflame gases, the temperature to which these particles are subjected as they traverse this zone, and the degree to which they are subjected to oxidizing or reducing environment.

Perhaps one of the most important classes of particles produced are those with diameters of 0.01-0.04 microns. These small particles are termed combustion nuclei. Recent studies⁷⁶ have shown that they are produced by both premixed and diffusion flames. Furthermore, in the case of premixed flames they are emitted by lean as well as by rich flames.

Much is still unknown about the nature of these particles. For example, it is not known whether they form early in the combustion process and are partially consumed in the later stages of combustion, or whether their formation occurs in the post flame gases. Moisture does appear to greatly increase their concentration.⁷⁶ Also, their exact chemical composition is as yet unknown. Conceivably they could be mostly moisture-condensed on relatively stable flame ions that persist into the postflame gases. Alternatively, they could also result from reactions of acetylenic-type intermediates also present in the flame. In this latter case they would be composed largely of carbon and hydrogen. They are of particular interest because it is these small combustion nuclei that appear to coalesce or coagulate in the atmosphere to produce particles 0.1-0.5 microns in size. It is these latter particles that produce noticeable light scattering in the atmosphere.

Finally, since conditions that give carbon and carbonaceous smoke or "haze" in the atmosphere will also favor the passage of other unburnt organics they should be prevented.

How is organic (carbon) particulate matter to be avoided? The requirement is to approach, as closely as is possible, an equilibrium oxidation in the incinerator. According to Ross⁷⁷ gas and liquid fired incinerators must demonstrate that they are capable of approaching stoichiometric combustion using any fuel. A burner that gives complete combustion at zero excess air proves that it can achieve equilibrium. Time, temperature, and turbulence are all necessary parameters to achieve the desired thermodynamic results. For solid fuel incinerators it is often not practical to operate a unit at zero excess air. Designing solid waste incinerators, therefore, requires actual tests of the waste to be burned in the final type of incinerator that will be used. Model units of reduced size may be used.

Reactions in the Effluent Gases

In addition to the reactions occurring in precombustion, flame, and postflame regions, a myriad of other reactions occur subsequently in the effluent gases. The possibilities include reactions between gaseous species, condensation of materials, liquid or solid phase reactions in the condensed material, and reaction of gaseous or condensed material with the walls of the effluent container.

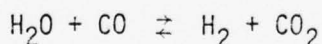
The components entering the effluent gases zone constitute a wide variety of species ranging from unreacted fuel to partially and completely reacted products.

Reactions between gaseous species may be illustrated with the following examples. Nitric oxide is the most stable oxide of nitrogen at the high temperatures encountered in combustion. At ambient temperatures nitrogen dioxide is the more stable oxide. Equilibrium considerations predict that when both oxygen and nitric oxide are present in the effluent gas, the nitric oxide will be oxidized to nitrogen dioxide as the gases cool. However, the rate is low and in most practical combustion devices, the general concentration of NO_2 is below 10 mole percent.

A similar situation is encountered in the case of sulfur oxides. The dioxide is stable at flame temperatures, whereas the trioxide is more stable at ambient conditions. Again, the homogeneous gas phase reaction of SO_2 with oxygen is too slow to produce much SO_3 .

Sulfur dioxide can react with carbon monoxide. The principal product of this reaction is CO_2 with some carbonyl sulfide (COS) and carbon disulfide (CS_2) also being produced.⁴²

The water-gas shift reaction



can produce an adjustment in the relative levels of CO , H_2 , H_2O , and CO_2 . The reaction will continue to occur so long as the temperature is sufficiently high. Once the level has dropped below a certain value, significant reaction ceases and the concentrations of the four species cited are essentially "frozen."

Some condensation reactions may be illustrated as follows. Water is one of the major products of the combustion of fossil fuels. Depending upon the equivalence ratio and the fuel composition anywhere, from less than a half to more than two pounds of water per pound of fuel burned may be generated, Figure 6.C-22.⁷⁸ The condensation of water vapor will occur if the temperature of the effluent gas drops to or below the dew point (point at which the gas is saturated with water vapor).

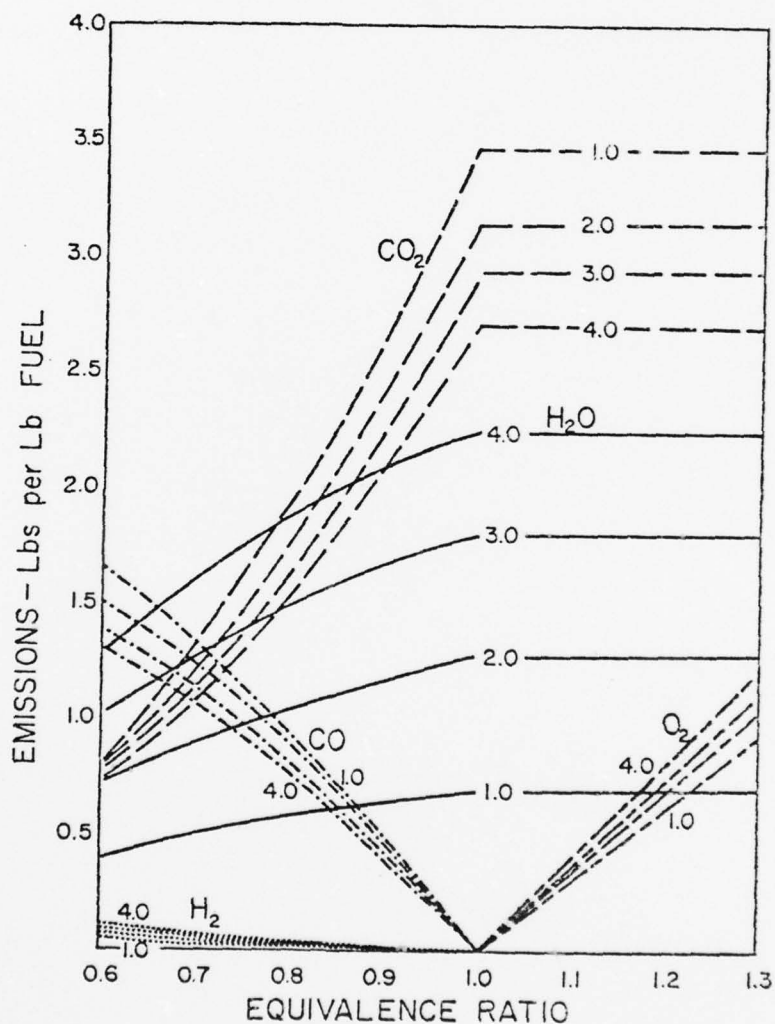


Figure 6.C-22 Weight of emission products per pound of fuel for hydrocarbon combustion. Equivalence ratio computed from air-fuel ratios.⁷⁸

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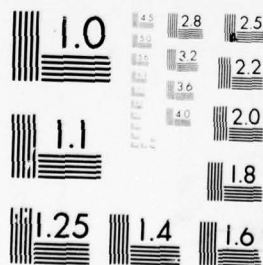


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Another example of a condensation reaction is the reaction of sulfur trioxide with water. In the reaction with water vapor, sulfur trioxide forms sulfuric acid. The temperature where this must first form as the gases are cooled is called the acid dew point. The acid dew point as a function of the sulfur trioxide concentration in the effluent gases is depicted in Figure 6.C-23.⁷⁹ The figure also shows the weight percentage of acid in the condensate and a measure of corrosiveness of this

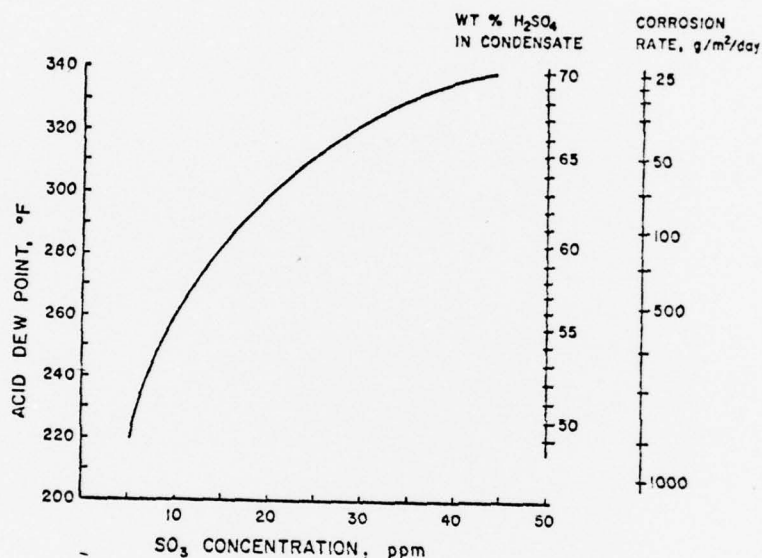


Figure 6.C-23 Acid dew point.

condensate on steel. Dilute acid is more corrosive than more concentrated acid. The presence of even small amounts of sulfur trioxide produces rather large increases in the dew point temperatures and, thus, in order to minimize corrosion, temperatures of the effluent gases should be kept high.

Finally, water is not the only condensable substance in effluent gases. Hydrocarbons and other organic species may form liquids, waxes or even solids as a result of condensation reactions. Certain fuel additives, especially those containing metallic compounds, may be vaporized or sublimed and will then later condense and deposit on the surfaces of the

system. Control and maintenance of high effluent temperatures is one method for minimizing such condensation effects.

The reactions with surface effects are more varied and complex and have not been delineated in any great detail. The process of deposition and agglomeration of particulate matter in effluent gases is one such topic. These effects, for example, are responsible for the non-coincidence in the rate of emission of the elements in the particle (mass/unit time) with the rate of ingestion of the same elements in the fuel. They are ingested continually with the fuel but their concentration appears as pulses or spikes in the effluent. In such cases, a mass balance cannot be obtained over the entire combustion process unless the averaging is done over a long period of time and a sufficient number of operating conditions. These effects are apparently due to large particle growth on the surfaces of the system and their periodic dislodgment and release in the effluent. In at least one case the mechanism for such large particle growth may be understood. When an acid mist (H_2SO_4) deposits on a metallic surface and corrodes it, a metallic sulfide (sulfate) is formed. This sulfide can now absorb both carbonaceous material and more SO_x until it has grown large enough to be dislodged. Thus this problem will be most likely to occur with fuels that contain significant quantities of sulfur.

Incineration

Incineration is a combination of pyrolysis and oxidation. Pyrolysis is the chemical change resulting from the action of heat alone. It involves bond-breaking processes, either to give free radicals or small molecules and remnant products. The trend is to small molecules, on the one hand, and to condensed products, ultimately carbon, on the other. Oxidation involves the gross reaction of the organic species of interest with oxygen. The organic species can be either the starting feed, or can be any of the pyrolytic or oxidatively produced intermediates. The reactivity of oxygen involves a variety of forms:⁶²

Molecular oxygen
Hydroxyl radical ($\text{HO}\cdot$)
Hydroperoxy radical ($\text{HOO}\cdot$)
Alkoxy radical ($\text{RO}\cdot$)
Alkylperoxy radical ($\text{ROO}\cdot$)
Other less reactive oxygen containing compounds
(hydroperoxides, peroxides, aldehydes, ketones,
alcohols, acids, and esters).

In oxidation the hydroxyl radical $\text{HO}\cdot$ is usually considered the chain carrier or most reactive species. Because of its high reactivity, and the high reactivity of other related species in oxidation, it is generally a much faster process than is pyrolysis. In kinetic terms, pyrolysis is a first order process requiring breaking of stable bonds, while oxidation is a second-order, branching process, where most steps are of relatively low activation energy since new bonds are forming as old bonds are broken. In approximate terms, oxidation occurs on a millisecond time scale while pyrolysis is on a time scale of seconds.

Accordingly, for efficient incineration, oxidation should be the dominant process, and pyrolysis should occur either incidentally to the oxidation, or to put a material into a better physical form for oxidation. Where materials do not oxidize readily on their own, whether due to low concentration, to low intrinsic heat of combustion (as perchloro-bodies), to intrinsically low rates (as carbon), or to inhibitory substances present (as halogens, phosphorus), auxiliary fuels have to be used to increase the rate by increasing the temperature and the concentration of reactive intermediates. The reactive intermediates in oxidation react only by colliding with adjacent molecules. This requires good mixing on a molecular scale for optimum rates, and accordingly, has a large impact on incinerator design.

Structural Effects

No detailed body of information exists that would permit one to predict the conditions for efficient incineration by inspection of the structure of the substance to be incinerated. The Environmental Protection Agency has classified wastes into four classes according to the elemental composition:⁶⁴

WASTE CLASS

1	C, H, and/or C, H, O
2	C, H, N, and/or C, H, N, O
3	C, H, Cl, and/or C, H, Cl, O C, H, Cl, N, and/or C, H, Cl, N, O C, H, S, and/or C, H, S, O
4	C, H, F, and/or C, H, F, O C, H, Br, and /or C, H, Br, O C, H, P, and/or C, H, P, O C, H, Si, and/or C, H, Si, O C, H, Na, and/or C, H, Na, O

The classification was presumably based on increasing severity to achieve equilibrium products in the oxidation sequence.

Based on generally known rates of pyrolysis and oxidation, some other relations can be used for classification. Aliphatic systems, for example, are more reactive than aromatic systems. Molecules without negative substituents (as halogens, acid groups, sulfur, possibly nitro groups) are more reactive than molecules with them. Single ring systems are more reactive than condensed ring systems.

Achievement of an equilibrium oxidation is of primary importance in incineration. If an oxidation is carried through to completion, the products will be small molecules, usually 2-3 atoms each (as H_2O , CO , CO_2 , SO_2 , NO , HCl) representing the most stable or equilibrium species at existing conditions, including temperature. In practice, conditions fluctuate throughout the oxidation zone, so that different portions of feed experience different conditions. Some feed may bypass much of the oxidation zone, and be only partially pyrolyzed instead. Contact times or mixing may not be long enough to reach an equilibrium state, so that pyrolysis and partly oxidized materials can be present, along with unchanged starting material.

When elements other than C, H, and O are present, the equilibria involved become more complex, since halogen, nitrogen, sulfur, and other elements modify the original systems, and are part of their own subsets. Specifically, pairs such as $NO-NO_2$, $HCl-Cl_2$, and SO_2-SO_3 become important.

Operating Variables in Incineration Performance

Temperature

Temperature is the resultant of two factors--the heat content or heat of combustion, and the rate of reaction, or heat release rate. Heat release rate is usually given in $\text{Btu/ft}^3/\text{hr}$. And since rate increases with temperature, a high heat content process with adequate rates at one temperature quickly becomes a high rate process at a higher temperature. The sharpness of the temperature peak and overall rate increase is limited by heat loss via radiation and transport, as one factor, and by the thermodynamic tendency for average molecular size to become small as temperature increases, so that less heat is available for further temperature increase.

There are two primary effects that the temperature determines: (1) the composition at equilibrium, and (2) the rate of all processes. Since each simple reaction has a different rate response to temperature change, the complex interaction sequence can give quite different intermediate product patterns over the range of temperatures encountered. The kinetic aspects of burning (or heat release rate) are very important. For a given fuel, the higher the release rate the higher the peak temperature will be, and presumably the closer to equilibrium the products will be. Operation under pressure will also increase release rate, but is rarely used. Essenhigh reviewed the general question of burning rates in incinerators, and noted that medium fuel oils could be fired at rates in the hundred thousands of $\text{Btu/ft}^3/\text{hr}$, and coal is generally fired at no more than 35,000 $\text{Btu/ft}^3/\text{hr}$.⁶⁵

Contact Time

Implicit in considerations of heat release rate is the question of how fast a fuel burns, or is subsequently oxidized after leaving the flame. The combustion process is accordingly divided into a primary zone, where active, flame-type burning proceeds, and a secondary (holding or retention) zone wherein hot gases are kept hot long enough to permit conversion of residual substances. If the primary zone doesn't approach equilibrium, the retention zone needs to be longer.

Exposure time in the primary zone is determined by flame volume and fuel/air mass flows, with flame volume being determined by a combination of flow rates and flow configurations and partly by heat release rates resulting from the intrinsic kinetics.

Exposure in the secondary or retention zone is determined by the size of the chambers beyond the active flame, and the mass flow rate through the chamber. Such times range from 0.5 to 5-10 seconds, depending on equipment and waste source.

If primary burning is effective, and products are close to equilibrium, then retention times needed should be small. An efficient burner corresponds to low hold times. Where hot retention is necessary, air addition to increase O_2 levels promotes oxidation and should be provided.

Excess Air

Air in excess of stoichiometric concentration serves two primary purposes: (1) to increase the concentration of oxygen and thereby the rate of combustion, and (2) to moderate maximum temperature by dilution and thereby reducing the rate of combustion. A balance of these two effects usually needs to be worked out.

Another important effect of excess air is to shift the product distribution. Limited data, however, are available on such effects as equilibrium concentrations.

Turbulence

Local variations of fuel and air concentration during the mixing process give rise to fuel rich zones and an excess of pyrolysis and condensation products to carbonaceous solids. An efficient incinerator avoids this through fast mixing by high turbulence.

Turbulence can be introduced by mechanical and aerodynamic means. Mechanical means are oldest, and least effective. Present practice with good results uses cyclonic or vortex combustion to produce radial motion with high shear. Fluid bed systems are described with good turbulence reported. Maximum turbulence is obtained at maximum air flow rates, and intermittent operation at full firing rates may be best for turn-down needs.

Minor Performance Factors

A list of minor performance factors is given below:⁶²

- Use of auxiliary fuel and reheat
- Quenching Control
- Bypass Control
- Back-mixing Control
- Turn-down Effects
- Lining heat retention and durability
- Burner on-time and shut-off efficiency
- Use of Pretreatment
- Use of Additives

These factors are mostly expressions of problems that can prevent attainment of adequate temperature, time, and turbulence.

A high heat load, or inadequate heat content, will usually require provision for auxiliary fuel feed. Typical systems would be those with high water content, with highly chlorinated materials, or with low concentration of organic vapors.

If the flame or hot gases touch a cool surface, as a wall, temperature drops and oxidation slows or stops. This quenching is a primary source of tars, condensates, and non-equilibrium products. The insulating lining surface should heat quickly, and retain heat well. The lining should also have reasonable thermal conductivity to reduce the likelihood of surface fusion.

Bypass effects occur when mixing is incomplete, and fuel rich feed bypasses the hot, oxidative zone. These organic species give rise to starting material in flue gas, as well as partly oxidized products and tars.

A variant of bypassing occurs when flue gases back-mix and dilute the oxygen supply so that oxidation is less complete.

Turn-down can reduce the effectiveness of mixing and of heat release rate, both because velocities are lower and because fuel supply is reduced. Accordingly, provision for maintaining mixing on turn-down must be worked out.

Related to the quench problem is the necessity of having a lining that will withstand the thermal-shock and temperature of operation and cycling. If the lining fails, then quenching can increase.

Burners operate most efficiently when continuously on. Intermittant operation means temperature cycling, and associated quenching and bypassing while the flame zone is being reestablished following ignition. Both effects increase non-ideal operation. If burner shutoff is slow, then fuel leakage from the feed system will give emissions, since the flame is gone.

Fuel pretreatment for liquids may include such processes as producing the proper viscosity of feed, removal of obstructing solids, or diluting with auxiliary fuel.

Additives have been used in boiler fuels to reduce smoke and soot; however, no reports have been found of their use in incinerators.

In summary, the available data in the literature indicate that an incinerator designed to provide 2700°F (1482°C) for 1.5 seconds would destroy most any hazardous material to be considered. However, this would be true only if all of the major and minor performance factors were also taken care of.

6.C.1.5 Conclusions

General Comments

1. Open burning of explosives and propellants should be discontinued as soon as possible because of the potential of generating large quantities of toxic combustion products.
2. In general, only a limited amount of information could be found on explosives and propellants combustion products.
3. Computer modelling is a desirable approach to optimizing incinerator operation and minimizing pollutant emissions.

Specific Comments

Information Available

Information on the total number of DOD facilities handling explosives and propellants, the total amounts of explosives and propellants combusted, and a limited amount of available emission factors has been assembled to permit the construction of a national DOD explosives emissions picture.

Open Burning

Some of the items (plastics, paper, textiles, wood) among the common military packaging materials are also items that have been open burned by municipalities. U. S. Public Health Service has pollutant sampling data that show that polycyclic aromatic hydrocarbons (twelve identified, many carcinogenic) are generated in such burning. Furthermore, Ringelman readings on explosives contaminated waste showed that Ringelman No. 4 (80 percent opacity) readings may exist for periods up to 18 minutes in some burns. The implications of these results are that significant concentrations of carcinogenic materials may be generated in the open burning of explosives and propellants contaminated waste as well as in the burning of the explosives themselves.

The open burning of waste explosives may also cause soil pollution especially in the disposal site area. Ashes, unburned waste materials as well as combustion products may be scattered over the disposal site and its surroundings by wind, rain, seepage, and spillage. Some of these products, e.g., TNT, have been found to be toxic to soil bacteria and fungi. Since the ground within a 200 foot radius of the burning pads must be cleared of all ground cover, wind and water erosion of the disposal site may also be a problem.

If the total munitions compositions are taken into consideration then some additional air pollutants may arise that may be potentially hazardous. For example, in the open burning of pyrotechnic materials such materials as asbestos, chromium, lead, barium, bromine, chlorine, fluorine, phosphorus, selenium, strontium, and their various oxidation products may also be released.

Incineration

If one compares the combustion products of municipal incinerators with those of open burning there appears to be little difference. Although this does not reflect favorably upon the particular incinerator efficiency or the mode of their operation, it does caution one that just because an Air Curtain, a Rotary Kiln, or a Rotary Furnace incinerator is being used it does not automatically mean that the only combustion products are always simple oxides of the elements in the fuel. Thus, a more detailed and extensive testing of incinerator combustion products is needed.

The limited amount of incineration work that the Army has done to date with pollution abatement equipped incinerators does indicate that there are at least two systems, SITPA II and the Rotary Kiln of RAAP, that would meet the existing emissions standards and would presumably eliminate the other objectionable emissions. Having seen both systems, we would favor the SITPA II over the Rotary Kiln on grounds of economics and ease of operation.

Computer Modeling of Combustion

Under ideal combustion conditions, i.e., equilibrium oxidation, CO_2 , CO , H_2O , NO , NO_2 , and SO_2 should be the only combustion species formed from materials containing only C, H, O, N, and S. However, under actual combustion conditions, a host of additional species are emitted. Presumably a computer program, developed by the Air Force Rocket Propulsion Laboratory at Edwards Air Force Base, California and adapted by the Ammunition Equipment Office, Tooele Army Depot, Tooele, Utah, can simulate furnace (incinerator) operating conditions and predict what combustion products may exist at furnace stack exit. Thus, given a certain furnace configuration and fuel composition, the computer model can determine the fuel and air feed rates and temperatures required to approach equilibrium oxidation conditions. Having discussed the thermochemistry computer program capabilities with Edwards Air Force Base personnel and having analyzed a limited TNT computer modelling data set, we strongly suggest that a much more expanded effort be undertaken in this direction with the objective of optimizing incinerator operations.

6.C.1.6 Data Gaps

1. A more complete accounting of combustion products generated in the open burning of explosives and propellants is needed.
2. A more complete accounting of combustion products generated in the incineration of explosives and propellants is needed.
3. A strong effort in computer modelling of combustion product generation in the incineration of explosives and propellants is needed.

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APPENDIX 5

COMMON MILITARY PACKAGING MATERIALS AS POTENTIAL EXPLOSIVES CONTAMINATED MATERIALS⁴

Category/Name	Common Name (Form)	Use	Fed/Mil. Specs.
Acetone	Acetone (Liquid)	Solvent	O-A-51
Benzene	Benzol (Liquid)	Solvent	VV-B-231
Carbon Tetrachloride	Carbon Tetrachloride (Liquid)	Solvent	
Corrosion Preventive	Corrosion Preventive	Perservative	Mil-C-6529 Mil-C-15074 Mil-C-16173 Mil-C-81304 Mil-C-11796
Corrosion Preventive	Dessicant (Powder)	Dehydrating Agent	Mil-D-3464
Corrosion Preventive	Oil Type Volatile Corrosion Inhibitor (Fluid)	Perservative	Mil-I-23310
Corrosion Preventive	VCI (Solid)	Perservative	Mil-I-22110
Detergent	Alkali Cleaning Compound (Liquid)	Detergent	P-C-436
Detergent	Detergent (Liquid)	Detergent	Mil-D-16791
Grease	Grease (Fluid)	Perservative	Mil-G-7711 Mil-G-23827 Mil-G-10924
Lubricating Oil	Lubricating Oil (Liquid)	Perservative	VV-L-800 Mil-L-3150
Methanol	Wood Alcohol (Liquid)	Solvent	O-M-232
Petrolatum	Petrolatum (Liquid)	Perservative	Mil-C-10382
Petroleum Cleaning Solvent	Stoddard Solvent	Solvent	P-D-680

Category/Name	Common Name (Form)	Use	Fed/Mil. Specs.
Petroleum Distillate	Mineral Spirits (Liquid)	Solvent	TT-T-291
Tetrachloroethylene	Perchloroethylene (Liquid)	Solvent	O-T-236
Trichloroethylene	Perchloroethylene (Liquid)	Solvent	O-T-634
GLASSES			
Glass	Fiberglass (Fiber)	Cushioning	Mil-C-17435
Glass/Plastic	Fiberglass (Sheet)	Containers, Trays	
Glass	Glass (Solid Rock)	Containers	
Mineral	Vermiculite (Fiber)	Cushioning	Mil-V-21628 Mil-V-23776
METALS			
Aluminum	Aluminum (Foil)	Trays, Wrapping	Mil-A-148
Aluminum	Aluminum (Sheet)	Cans, Tubes	QQ-A-250
Lead	Lead (Sheet)	Tubes	QQ-L-201
Steel, Iron	Metal Cylinders (Solid Stock)	Cylinders, Caps	
Steel, Iron	Metal Drums (Sheet)	Drums	PPP-D-705 PPP-D-711
Steel, Iron	Metal Strapping (Straps)	Strapping	QQ-S-781
Tin-Plated	Tin Cans	Cans	PPP-C-96 PPP-C-29
Tin-Plated Steel/Aluminum	Bimetallics	Cans	
Various Metals	Aerosols (Sheet)	Pressurized Cans	PPP-C-96
PAPERS			
Fiberboard	Coated Corrugated Containerboard (Sheet)	Containers	PPP-B-1608

Category/Name	Common Name (Form)	Use	Fed/Mil. Specs.
Fiberboard	Corrugated and Solid Board or Container-board	Containers	PPP-B-640 PPP-B-676 PPP-B-1364 PPP-B-636 PPP-B-320
Fiberboard	Wax Impregnated Corrugated Board (Sheet)	Containers	PPP-B-1163 Mil-C-3955
Paper	Bag and Sack (Sheet)	Bags, Sacks	PPP-S-30 UU-B-36 UU-S-48
Paper	Coated, Impregnated (Sheet)	Wrapping, Bags	Mil-P-20293 UU-P-134
Paper	Converting, Envelope (Sheet)	Envelopes Tapes	PPP-T-45
Paper	Newsprint (Sheets, Shreds)	Wrapping, Dunnage	
Paper	Pulp (Molded)	Trays	
Paper	Tissue (Sheet)	Wrapping	UU-P-553
Paper	VCI Treated Packaging (Sheet)	Containers	Mil-P-3420
Paper	Wax Paper (Shreds)	Wrapping Dunnage	
Paper	Wrapping (Sheet)	Wrapping, Bags	UU-P-268
Paperboard	Chipboard, Boxboard (Sheet)	Boxes	UU-C-282 PPP-B-566
Paperboard	Spirally Wound Fiber Can (Sheet)	Can	Mil-C-2439
Paper/Foil Lamination	Polyolefin-Foil-Paper (Sheet)	Wrapping, Barrier Material	Mil-B-131
Paperboard/Metal	Metal-edged Paperboard (Sheet)	Boxes	PPP-B-665
Paperboard/Metal	Metal-edged Paperboard (Sheet)	Drums, Tubes	PPP-D-723

Category/Name	Common Name (Form)	Use	Fed/Mil. Specs.
Fiberboard/Wood	Wood-cleated Fiber-board (Sheet)	Boxes	PPP-B-591
PLASTICS			
Acrylonitrile Buta- diene Styrene	ABS (Solid Stock, Sheet)	Trays Containers	L-P-1183
Cellulosics	Cellophane (Film)	Wrapping Bags	L-C-110
Cellulosics	Cellulose Acetate (Foam)	Cushioning	PPP-C-843
Cellulosics	Cellulose Acetate (Sheet, Film)	Wrapping	L-P-504
Cellulosics	Cellulose Acetate Butyrate (Solid Rock)	Containers	L-P-397 L-P-349
Cellulosics	Strippable Plastic Coating-Cold (Film)	Coating	Mil-P-45021
Cellulosics	Strippable Plastic Coating-Hot (Film)	Coating	Mil-P-149
Epoxy	Epoxy Resin (Film)	Coating	Mil-R-21931
Inomer	Surlyn (Film, Sheet)	Wrapping Molded Parts	Mil-P-46124
Inomer	Surlyn (Foam)	Cushioning	
Phenolics	Bakelite (Solid Stock)	Trays Containers	Mil-R-3745 L-P-1125
Plastic/Foil Lamination	Polyolefin/Aluminum/ Polyester, Marplex (Sheets)	Wrapping Pouches	
Polyacrylics	Lucite, Plexiglas (Solid Stock, Sheet)	Containers	L-P-507 Mil-P-8184
Polyamids	Nylon (Cloth)	Sacks	Mil-C-81268
Polyamids	Nylon (Fiber)	Cord	Mil-C-5040
Polycarbonate	Polycarbonate (Sheet)	Wrapping	Mil-P-46144 Mil-P-83310
Polycarbonate	Polycarbonate (Solid Stock)	Containers	

Category/Name	Common Name (Form)	Use	Fed/Mil Specs.
Polyester	Dacron (Fiber)	Straps	
Polyester	Mylar (Film)	Pouches	L-P-377
Polyolefin	Polyethylene (Film)	Wrapping Pouches	L-P-378
Polyolefin	Polyethylene (Solid Stock)	Containers	Mil-D-40030
Polyolefin	Polypropylene (Fiber)	Cord	Mil-R-24049
Polyolefin	Polypropylene (Film)	Wrapping, Pouches	L-P-378
Polyolefin	Polypropylene (Foam)	Cushioning	Mil-C-81823
Polyolefin	Polypropylene (Solid Stock)	Containers	L-P-393 L-P-394
Polystyrene	Polystyrene (Sheet, Film)	Wrapping	L-P-506
Polystyrene	Polystyrene (Solid)	Containers, Molded Parts, Sheeting	L-P-396
Polystyrene	Styrofoam (Foam)	Containers	
Polystyrene	Styrofoam (Foam)	Cushioning	PPP-C-850
Polystyrene	Styrofoam (Pellets)	Dunnage	Mil-P-19644
Polysulphone	Polysulphone (Solid Stock)	Trays, Containers	Mil-P-36120
Polytetrafluoroethylene	Teflon (Sheet, Film)	Wrapping	Mil-P-22241
Polytetrafluoroethylene	Teflon (Solid Stock)	Containers	L-P-403
Polyurethane	Polyurethane (Film)	Wrapping	Mil-P-43604
Polyurethane	Polyurethane (Foam)	Cushioning	Mil-P-26514
Polyurethane	Polyurethane (Solid Stock)	Containers	Mil-M-24041 Mil-C-38226
Polyvinyl Alcohol	PVA (Sheet)	Wrapping	
Polyvinyl Alcohol	PVAC (Sheet)	Wrapping	L-P-535

Category/Name	Common Name (Form)	Use	Fed/Mil. Specs.
Polyvinyl Chloride	PVC (Film)	Wrapping Pouches, Waterproof Covers	L-P-375
Polyvinyl Chloride	PVC (Solid Stock)	Containers, Blister Pack- ages, Liners	L-P-535
Polyvinylidene Chloride	Saran, PVDC (Film)	Wrapping	L-P-370
Rubber	Latex (Foam)	Cushioning	Mil-R-5001
TEXTILES			
Bound Fiber	Rubberized Hair (Fiber)	Cushioning	PPP-C-1120
Canvas, Rubberized	Tarp (Cloth)	Tarpaulin	
Cotton	Cotton (Cloth)	Cushioning	
Cotton	Cotton (Cloth)	Rags	
Cotton	Cotton (Cloth)	Sacks	PPP-B-1358 PPP-B-1087
Felt	Felt (Sheet)	Cushioning	C-F-202 C-F-206
Jute	Burlap (Cloth)	Sacks	PPP-B-35 CCC-C-467
Scrim/Foil Lamination	Polyolefin/Aluminum/ Scrim (Sheet)	Barrier	Mil-B-131
WOODS			
Wood	Cooperage (Board)	Kegs	NN-K-231 PPP-B-41
Wood	Excelsior (Shreds)	Dunnage	PPP-E-91
Wood	Plywood (Sheet)	Crates	NN-P-530
Wood	Veneer (Sheet)	Crates	PPP-V-205
Wood	Wood (Board)	Crates Pallets	PPP-B-621 Mil-P-3938
Wood/Metal	Nailed or Wirebound (Board)	Crates Pallets	PPP-B-585 PPP-B-587

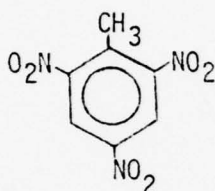
APPENDIX 6

COMPOSITION AND/OR CHEMICAL STRUCTURE OF MATERIALS BURNED

Explosives and Propellants Components

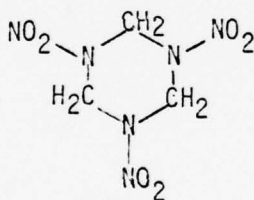
PURE COMPOUNDS

2,4,6-Trinitrotoluene, TNT



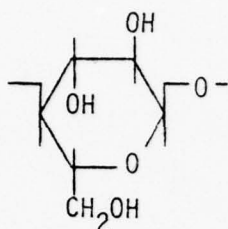
RDX (Cyclonite, Hexogen, T₄, C₆, trimethylenetrinitramine, 1,3,5-trinitro-1,3,5-triazacyclohexane)

RCA (RDX, Class A of a specific particle size distribution)



Desensitized RDX-RDX plus wax (1-2%)

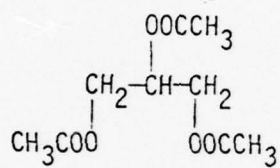
Starch (Amylose)



Sulfur



Triacetin

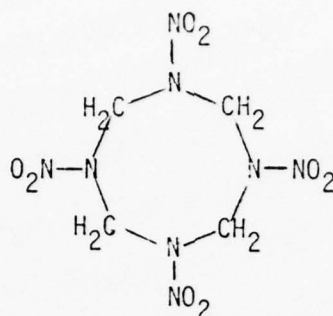


Wood's Metal

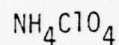
Bi/Pb/Sn/Cd

50% 25% 12.5% 12.5%

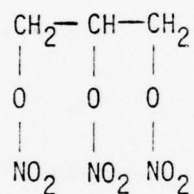
HMX (homocyclonite, Octogen, Hexamethylenetetranitramine, 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane)



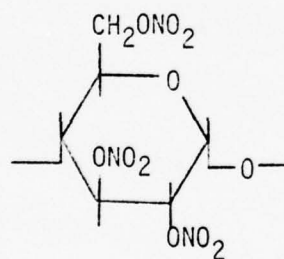
Ammonium Perchlorate



Nitroglycerin, NG, TNG, Glyceryl Trinitrate

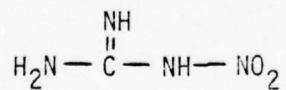


Nitrocellulose, NC (12.6% N - 14.14% N), Cellulose Nitrate

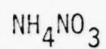


C	24.25%
H	2.37%
N	14.14%
O	59.24%
C/H	0.23

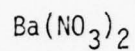
Nitroguanidine



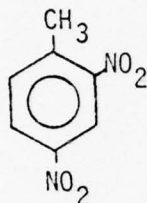
Ammonium Nitrate



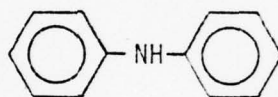
Barium Nitrate



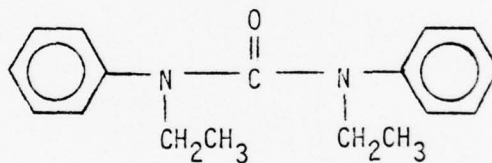
Dinitrotoluene



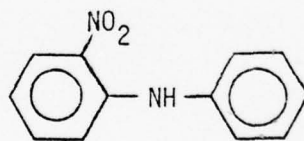
Diphenylamine



Ethyl Centralite (N,N'-Diethyl-N,N'-diphenylurea)



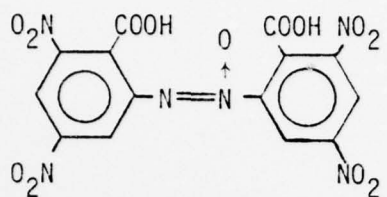
2-Nitrodiphenylamine



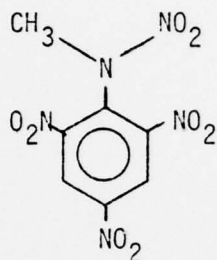
Potassium Nitrate



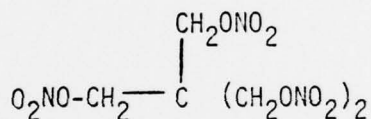
"White Compound" - 2,2'-Dicarboxy-3,3',5,5'-tetrinitroazoxybenzene



Tertyl (2,4,5-trinitrophenylmethylnitramine)



PETN (pentaerythritol tetranitrate)



Composite Explosives

Single-base propellants (IMR, M12, M1 MIL-P-309A)--

NITROCELLULOSE AND ITS MINOR MODIFICATIONS COMPOSITIONS

IMR Type Powder

Nitrocellulose (13.15% N)	89.89%
Dinitrotoluene	8.76%
Diphenylamine	0.62%
K ₂ SO ₄	0.43%
Total Volatiles	0.82%
Moisture	0.80%

M12

Nitrocellulose (13.15% N)	97.70%
Dinitrotoluene	8.00%
Ethyl Alcohol (Residual)	1.50%
Water (Residual)	1.00%
Diphenylamine	0.80%
Tin	0.75%
K ₂ SO ₄	0.75%

M1 MIL-P-309A

Nitrocellulose (13.15% N)	85.00%
Dinitrotoluene	10.00%
Dibutylphthalate	5.00%
Diphenylamine	1.00%
Ethyl Alcohol (Residual)	0.75%
Water (residual)	0.50%

Double-base propellants (Ballistite JP204, BDI, T25, ABL)--

NITROCELLULOSE AND NITROGLYCERIN COMPOSITIONS

Ballistite JP204

Nitrocellulose (13.2% N)	51.6%
Nitroglycerin	43.0%
Diethylphthalate	3.25%
KNO ₃	1.4%
Diphenylamine	0.75%
Methyl Cellulose	0.16%

BDI

Nitrocellulose (12.6% N)	38.5%
Nitroglycerin	44.9%
Triacetin	12.4%
Lead Oxide	3.2%
2-Nitrodiphenylamine	1.0%

ABL

Nitrocellulose (12.6% N)	60.0%
Nitroglycerin	28.0%
Triacetin	6.0%
Lead Oxide	5.0%
2-Nitrodiphenylamine	1.0%
Graphite	0.05%

T25

Nitrocellulose (13.15% N)	73.25%
Nitroglycerin	20.0%
Ethyl Centralite	5.0%
Ethyl Alcohol (Residual)	1.20%
Ba(NO ₃) ₂	0.75%
KNO ₃	0.70%
Water (Residual)	0.50%
Graphite	0.30%

Triple-base propellants (M17, T20, M31)--

NITROCELLULOSE, NITROGLYCERINE, AND NITROGUANIDINE COMPOSITIONS

M17

Nitrocellulose (13.15% N)	22.00%
Nitroglycerin	21.50%
Nitroguanidine	54.70%
Ethyl Centralite	1.50%
Ethyl Alcohol (Residual)	0.30%
Cryolite	0.30%
Graphite	0.10%

T20

Nitrocellulose (13.15% N)	20.00%
Nitroglycerin	13.00%
Nitroguanidine	60.00%
Dibutylphthalate	5.00%
Ethyl Centralite	2.00%
Lead Carbonate	1.00%
Ethyl Alcohol (Residual)	0.30%

M31

Nitrocellulose (12.60% N)	20.00%
Nitroglycerin	19.00%
Nitroguanidine	54.70%
Dibutylphthalate	4.50%
Diphenylamine	1.50%
2-Nitrodiphenylamine	1.50%
Cryolite	0.30%
Ethyl Alcohol (Residual)	0.30%

Composite modified double-base propellants (EDX)--

A solvent-extruded composite propellant composition is illustrated below:

KNO ₃	43.00%
Nitrocellulose	23.00%
Nitroglycerine	22.00%
Carbon Black	7.00%
Ethyl Centralite	5.00%
Magnesium Stearate	0.6%

LEW (Liquid Explosive Wastes)--

Liquid explosives wastes can be quite a complex mixture of different chemical species, however, the most common major components are:

Nitroglycerin
Cellulose (saw dust)
Triacetin (glyceryl triacetate)
Sodium sulfide
Water

RDX-based explosive mixtures--

Composition A-3

RDX 91
Wax 9

Composition A-4

RDX 97
Wax 9

Composition A-5

	<u>Type I</u>	<u>Type II</u>
RDX	98.5-99.0%	98.0%
Stearic acid	1.0-1.5%	1.6%
Graphic with Ca resinate	---	0.4%

Composition B

RDX	60%
TNT	40%
Wax	1%

Composition B-4

RDX	60%
TNT	39.5%
Ca silicate	0.5%

Cyclotols

	<u>75/25</u>	<u>70/30</u>	<u>65/35</u>
RDX	75%	70%	65%
TNT	25%	30%	35%

Composition C-3

RDX	77%
Dinitrotoluene	10%
Mononitrotoluene	5%
TNT	4%
Tetryl	3%
Nitrocellulose	1%

Composition C-4

RDX	91%
Di(2-ethylhexyl) sebacate	5.3%
Polyisobutylene	2.1%
Motor Oil	1.6%

Composition H-6

RDX	45%
TNT	30%
Aluminum	20%
Composition D-2	5%
Calcium Chloride	0.5%

Composition D-2

Wax	84%
Lecithin	2%
Nitrocellulose	14%

Black Powder (Benite)

Nitrocellulose (13.15% N)	40.8%
KNO ₃	44.3%
Charcoal	9.4%
Sulfur	6.3%
Ethyl Centralite	0.5%

Smokeless Powder

Nitrocellulose (13.15% N)	81.4%
Nitroglycerin	10.0%
Dibutylphthalate	7.6%
Diphenylamine	1.0%

PBX's

Type A

RDX	90.0%
Polystyrene	8.5%
Diethylphthalate	1.5%

Type B

RDX	89.9%
Gum Resin	4.4%
Polystyrene and a Dye	5.7%

N-1

RDX	69%
Aluminum	20%
Zytel 63	12% (Nylon copolymers and a plasticizer)

N-3

HMX	85%
Zytel 63	15%

9010

RDX	90%
Kel F elastomer	10% (Contains fluorine and chlorine)

9404

HMX	94%
Tris(β -chloroethyl)phosphate	3%
Nitrocellulose	2.9%
Diphenylamine	0.1%

Tritonal

TNT	80%
Aluminum	20%

HBX-1

RDX	40%
TNT	38%
Aluminum	17%
Composition D-2	5%
CaCl ₂	0.5%

Pentolite 50/50

PETN	50%
TNT	50%

Minol-2

NH ₄ NO ₃	40%
TNT	40%
Aluminum	20%

Octol 75/25

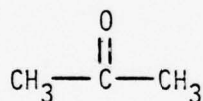
HMX	75%
TNT	25%

High Energy Propellants

Various other high energy propellant formulations consisting of nitrocellulose, nitroglycerin, ammonium perchlorate, aluminum, or HMX-RDX, aluminum or lead salt compositions are also burned at RAAP.²

Common Military Packaging Materials

Acetone



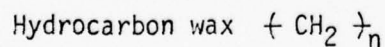
Benzene



Carbon Tetrachloride



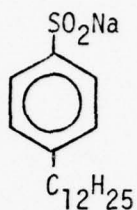
Corrosion Preventive



Detergent

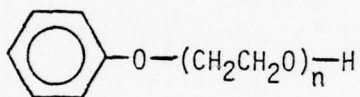
Ionic

Sodium salt of sulfonated and alkylated benzene



Non-Ionic

Monoaryl ethers of polyethylene glycols



Grease, Petrolatum, Lubricating Oil

Hydrocarbons $\leftarrow \text{CH}_2 \rightarrow_n$

Stoddard Solvent, Mineral Spirits

Hydrocarbons $\leftarrow \text{CH}_2 \rightarrow_n$

Methanol

CH_3OH

Tetrachloroethylene

$\text{Cl}_2\text{C}=\text{CCl}_2$

Trichloroethylene

$\text{ClHC}=\text{CCl}_2$

Glass (Fiberglass, E Glass)

SiO ₂	54%
CaO	18%
Al ₂ O ₃	14%
B ₂ O ₃	8%
MgO	5%
Na ₂ O/K ₂ O	0.5%

Vermiculite Fiber (Montana Ore)

Hydrated magnesium-aluminum-iron silicate, typical composition:

SiO ₂	38.65%
MgO	22.68%
Al ₂ O ₃	14.94%
Fe ₂ O ₃	9.29%
K ₂ O	7.84%
CaO	1.23%
Cr ₂ O ₃	0.29%
Mn ₃ O ₄	0.11%
[Cl]	0.28%

Fiberboard

Cellulose
Clay
Adhesives
Resin Coating and Binder

Paper

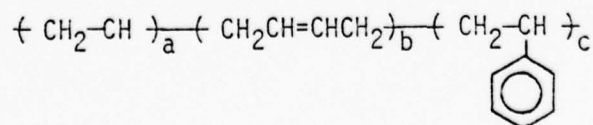
Cellulose
Clay
Resin Binder

Paperboard

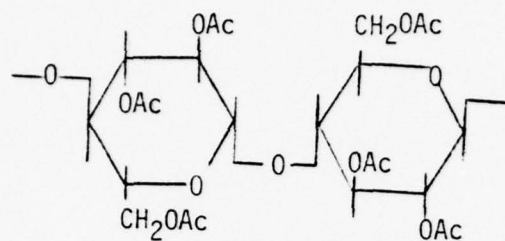
Cellulose
Clay
Resin Binder
Adhesives

ABS Plastics

Acrylonitrile/Butadiene/Styrene Resins



Cellulosics - Cellulose Acetate

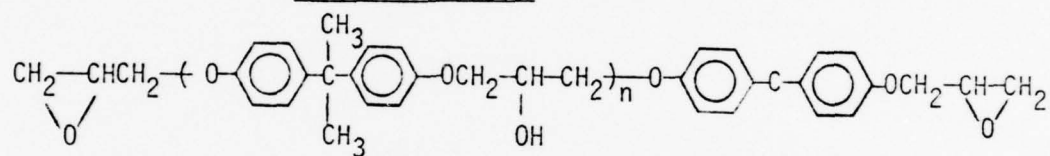


Cellophane

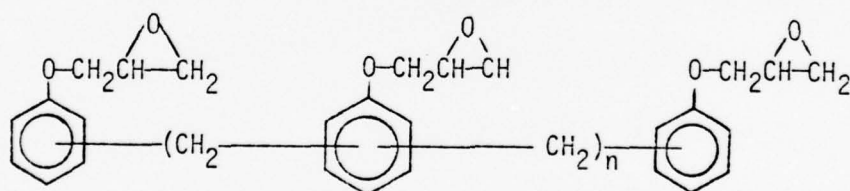
Cellulose

Epoxy Resins

Bisphenol A Type

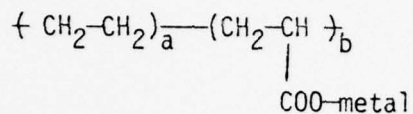


Epoxidized Novolak Type



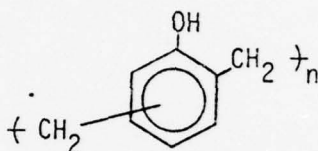
Inomers (Surlyn)

Copolymers of unsaturated hydrocarbons and salts of unsaturated acids; most common commercial product--ethylene/salt of acrylic acid copolymer



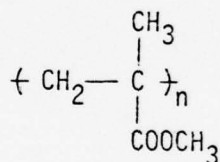
Phenolics

Phenol/Formaldehyde Resins



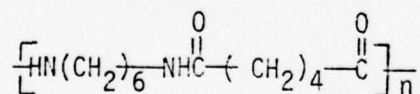
Polyacrylics (Lucite, Plexiglass)

Polymethyl Methacrylate



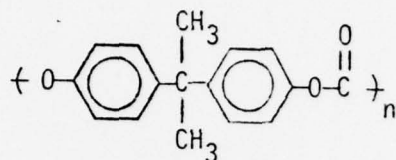
Polyamids (Nylon 66)

Condensation products of diamines and diacids, for example:



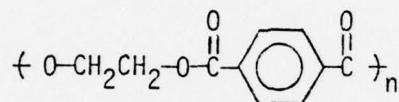
Polycarbonate (Lexan)

Polycarbonates are a special type of polyesters in which the aromatic or aliphatic dihydroxy groups are linked through carbonate groups:



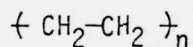
Polyester (Dacron, Mylar)

Condensation products of aromatic or aliphatic diols and aromatic or aliphatic diacids:

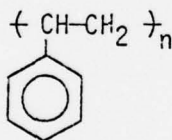


Polyolefins (Polyethylene, Polypropylene, etc.)

Polymers of unsaturated hydrocarbons:

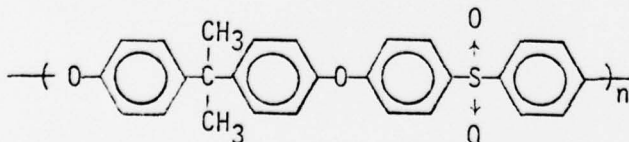


Polystyrene (Styrofoam)

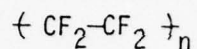


Polysulfone

Condensation product between the sodium salt of Bisphenol A and 4,4'-dichlorodiphenyl sulfone:

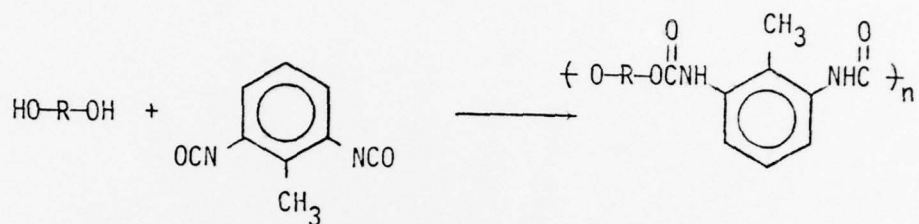


Polytetrafluoroethylene (Teflon)

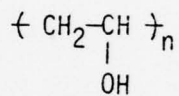


Polyurethanes

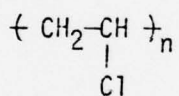
Condensation products between polyols with active hydrogens and diisocyanates:



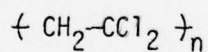
Polyvinyl Alcohol



Polyvinyl Chloride (PVC)

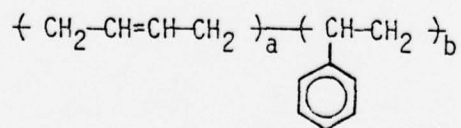
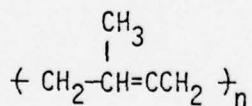


Polyvinylidene Chloride (Saran)



Rubber (Latex)

Polymers of unsaturated dienes or diene and styrene:



Rubberized Fibers

Cellulose
Protein (wool)
Synthetic polymer fibers coated with rubber

Cotton

Cellulose

Felt

A composite made of either:

Cellulose
Wool
Protein
Synthetic Fibers

Jute

Cellulose

Wood

Cellulose

Common Propellant Ingredients

Aluminum, Al

Acetone, see previous section

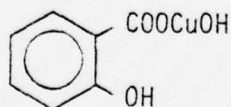
Benzene, see previous section

Carbon, C

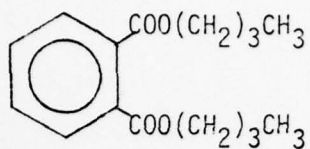
Cellulose, see previous section

Cellulose acetate, see previous section

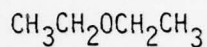
Cupric Salicylate (Monobasic)



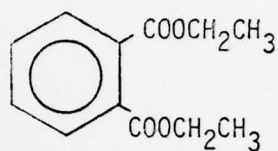
Dibutyl Phthalate



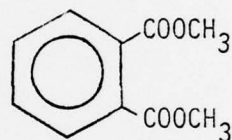
Diethyl Ether



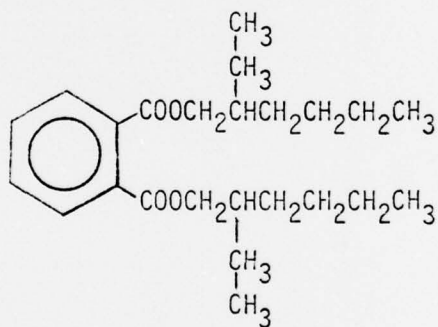
Diethyl Phthalate



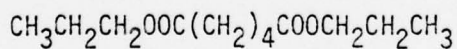
Dimethyl Phthalate



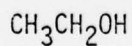
Di-octyl Phthalate



Di-n-propyl Adipate



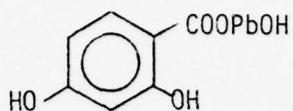
Ethyl Alcohol



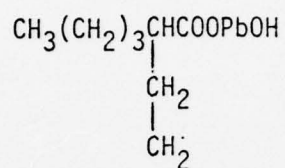
Lead Carbonate



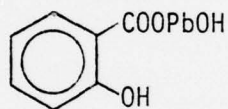
Lead-β-resorcylate (Monobasic)



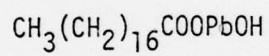
Lead-2-ethylhexoate (Monobasic)



Lead Salicylate (Monobasic)



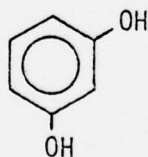
Lead Stearate (Monobasic)



Potassium Sulfate



Resorcinol



APPENDIX 7

THERMODYNAMIC DATA SOURCES ON CHEMICAL SUBSTANCES AND MATERIALS

The following references have been selected to provide a reasonably comprehensive coverage of thermodynamic data. Except for the Landolt-Börnstein Tables, foreign language compilations have not been included.

1. Ashcroft, S. J. and C. T. Mortimer, Thermochemistry of Transition Metal Complexes, Academic Press, London, New York, 1970.
2. Cox, J. D. and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, New York, 1970.
3. Domalski, E. S., "Selected Values of Heats of Combustion and Heats of Formation of Organic Compounds Containing the Elements C, H, N, O, P, and S", Journal of Physical and Chemical Data, 1, 221-227 (1972).
4. Hilsenrath, J., C. W. Beckett, W. S. Benedict, L. Fano, H. S. Hoge, J. F. Masi, R. L. Nuttall, Y. S. Touloukian, and H. W. Woolley, Tables of Thermal Properties of Gases, National Bureau of Standards Circular 564 (1955), U. S. Government Printing Office, Washington, D. C. 20402.
5. Hultgren, R., R. L. Orr, P. D. Anderson, and K. K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys, John Wiley and Sons, Inc., New York, 1963.
6. Kelley, K. K., Contributions to the Data on Theoretical Metallurgy XV. A Reprint of Bulletins 383, 384, 393, and 406, U. S. Bureau of Mines Bulletin 601 (1962). U.S. Government Printing Office, Washington, D. C.
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APPENDIX 8

ESTIMATED EMISSIONS OF PRIMARY^a AIR POLLUTANTS FROM THE OPEN BURNING OF WASTE EXPLOSIVES AND PROPELLANTS MATERIALS BY DOD DURING 1975¹

	ARMY		NAVY		AIR FORCE		TOTAL	
	Tons	Metric Tons	Tons	Metric Tons	Tons	Metric Tons	Tons	Metric Tons
Carbon Monoxide (CO)	166.6	151.1	56.6	51.3	4.2	3.8	227.3	206.2
Oxides of Nitrogen (NO _x)	445.3	404.8	151.6	137.5	11.3	10.2	609.2	552.5
Hydrocarbons	3.3	3.0	1.1	1.0	0.1	0.1	4.5	4.1
Particulates	535.6	485.8	181.9	164.9	13.5	12.2	731.0	662.9

^aThese air pollutants are emitted in the largest quantities from the open burning of waste explosives and propellants materials.

APPENDIX 9

ESTIMATED EMISSIONS OF AIR POLLUTANTS FROM THE OPEN BURNING OF EXPLOSIVES AND PROPELLANTS CONTAMINATED WASTES BY DOD DURING 1975¹

	EMISSION FACTOR	lb/ton	kg/mt	ARMY		NAVY		TOTAL	
				Tons	Metric Tons	Tons	Metric Tons	Tons	Metric Tons
Carbon Monoxide (CO)	85	42.5	1,112.3	1,008.9	18.4	16.7	1,130.7	1,025.6	
Oxides of Nitrogen (NO _x)	6	3	78.5	71.2	1.3	1.2	74.8	72.4	
Sulfur Oxides (SO _x)	1	0.5	13.1	11.9	0.2	0.2	13.3	12.1	
Hydrocarbons	30	15	392.6	356.1	6.5	5.9	399.1	362.0	
Particulates	16	8	209.4	189.9	3.4	3.1	212.8	193.0	

APPENDIX 10

LIST OF COMBUSTION PRODUCTS SAMPLED IN OPEN BURNING

A) Explosives and Propellants

O₂
N₂
CO
CO₂
NO_x
CH₄
HCl
HF
P₂O₅
Hydrocarbons
Particulates

B) Other Materials Burned

Pyrene
Benzo(a)pyrene
Benzo(e)pyrene
Perylene
Benzo(ghi)perylene
Anthanthrene
Coronene
Anthracene
Phenanthrene
Fluoranthene
Benz(a)anthracene
Chrysene
CO
CO₂
NO_x
Hydrocarbons
Formaldehyde
Organic Acids
Particulates

APPENDIX 11

LIST OF COMBUSTION PRODUCTS SAMPLED IN INCINERATION

A) Explosives and Propellants

N₂
 O₂
 CO₂
 H₂S
 NO
 NO₂
 SO₂
 Hydrocarbons
 HCl
 H₂SO₄
 Methane
 Ethane
 Ethylene
 Propylene
 Butylene
 Particulates
 Nitro bodies

B) Other Materials Incinerated

CO	Benz(a)anthracene	Chlorine
SO ₂	Chrysene	Methane
NO _x	Benzo(b)fluoranthene	Ethane
Hydrocarbons	Benzo(k)fluoranthene	Ethylene
HCl	Benzo(j)fluoranthene	Propane
Mineral Particulates	Indeno(1,2,3-cd)pyrene	Propylene
Particulates	HCN	iso-Butane
Volatile Metals	NO	n-Butane
Benzo(a)pyrene	CH ₃ CN	iso-Pentane
Pyrene	CS ₂	n-Pentane
Benzo(e)pyrene	H ₂ S	HF
Perylene	COS	"Phosphate"
Benzo(ghi)perylene	Pyrrole	
Anthanthrene	Phenol	
Coronene	Organic Acids	
Anthracene	Aldehydes and ketones	
Phenanthrene	COCl ₂	

APPENDIX 12

LIST^a OF COMBUSTION SPECIES GENERATED IN THE INCINERATION OF TNT AS PREDICTED
BY A COMPUTER MODEL (TNT/AIR 440; 1993°C)

• C	C ₂ O
CH	C ₃
• CHN	• C ₃ O ₂
CHNO	C ₄
CHO	C ₄ N ₂
CH ₂	C ₅
• CH ₂ O	H
CH ₃	HN
• CH ₄	HO
• CH ₃ OH	• H ₂
CN	• HCOOH
CN ₂	H ₂ N
CNN	H ₂ N ₂
• CO	• H ₂ O
• CO ₂	• NH ₃
C ₂	N
C ₂ H	• NO
• C ₂ H ₂	• N ₂
• C ₂ H ₄	O
C ₂ N	• C (graphite)
C ₂ N ₂	

^aAbove 10⁻¹² moles/100 g

•Molecular species

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